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CAMPHOROXALIC ACID DERIVATIVES. VI.

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INTRODUCTION.

IN the course of an investigation of the action of ethereal oxalates on aliphatic ketones,[1] it was found that the impure sodium camphor, obtained by the action of one atomic proportion of sodium on camphor, in boiling toluene solution, condenses with ethylic oxalate. The yield was extremely poor. At that time, the question of the presence in the camphor molecule of the group $—CH_2.CO—$ was an open one, and the first conclusive and direct proof of its occurrence was afforded by this work. Apart from the special interest which the subject thus acquired, it possessed other more general ones; hence, the investigation of the above condensation product, termed ethylic camphoroxalate, was continued at the Heriot-Watt College, Edinburgh.

The yield was improved materially and a number of derivatives prepared and studied. Pressure of other work caused the suspension of the research until 1897. During this interval, the point alluded to above, regarding the constitution of camphor, was generally recognized as settled, but other questions had arisen that appeared to make the extended investigation of camphoroxalic acid desirable. One of these concerned the true constitution of "diketones," of which ethylic camphoroxalate may be taken as an example: were they to be regarded as unsaturated

[1] Inaugural Dissertation., Munich University, 1889, p. 34.

keto-alcohols or as true diketones? From the almost neutral character of the camphor nucleus, and its relatively large mass, camphoroxalic acid appeared to be peculiarly well fitted for the purpose of investigation in this direction. A further object was to accumulate data which might elucidate to some extent the mechanism of the Claisen condensation. The work was therefore resumed at the University of Chicago, and has since been continuously prosecuted, first at the University of Pennsylvania, and subsequently in this laboratory. The results as regards the constitution of camphoroxalic acid are apparently complete, and indicate that it is an unsaturated keto-alcohol. In addition to this, a new class of compounds has been discovered, formed by the condensation of the acid with amines. Most of the observations which have been made have been published at intervals as the work proceeded; in the present paper, these scattered communications[1] are briefly coordinated, corrected where necessary, and a description is given for the first time of a series of compounds obtained by the action of camphoroxalic acid and ethyl camphoroxalate on ammonia and certain aliphatic amines.

THEORETICAL.

A number of experiments were made in order to determine the most suitable conditions for the preparation of camphoroxalic acid and its ethyl salt; these may be thus summarized: (1) Sodium with ethyl oxalate and camphor in boiling toluene; (2) Dried sodium ethoxide suspended in boiling ether; (3) Sodium ethoxide in absolute alcoholic solution; (4) Sodium wire with the camphor and ethyl oxalate in absolute ethereal solution; (5) Sodium wire as in 4, in dried, light petroleum solution. The results are as follows:

Experiment.	Molecules camphor to 1 molecule ethyl oxalate.	Atoms sodium.	Crude ethyl salt and acid per cent. of theoretical.	Acid formed per cent. of theory.	Acid 1 part: of ethyl salt.
1	2	2	small	....	....
2	1	1	10	....	....
3	1	1	4.4	....	....
4	1½	1	58.0	4.9	0.07
5*a*	1½	1	63.5	Ethylic salt only	
5*b*	1½	1	92.4	17.0	0.2
5*c*	2	2	66.5	44.6	1.8

[1] Inaug. Diss., Munich, 1889, p. 34; *J. Chem. Soc.* (London), 1890, 652; *Am. Chem. J.*, **19**, 393 (1897); *Ibid.*, **20**, 318 (1898); *Ibid.*, **21**, 238 (1899); *Ibid.*, **23**, 214 (1900).

It is immediately evident that the first three methods are quite unsuited for the preparation of the acid on a large scale. Experiments 4 and 5 show that the use of light petroleum is more favorable to the yield than that of ether, probably because of its higher boiling-point (about 70°); its cheapness, and the ease with which it can be dehydrated are also incidental, but highly important advantages. The influence of the varying amount of sodium is illustrated in experiments 5*a*, *b*, and *c*, the total yield is improved by the use of 1 atom to 1½ molecules of camphor, but a larger proportion of the latter favors the formation of acid at the expense of ethylic salt.

Recent research appears to indicate that, except in the case of hydrocarbons of the acetylene type, or those containing the linkage *C:C.C.C:C.*,[1] none of the organo-metallic compounds have the metal directly linked with carbon; accordingly, in formulating the above facts, Claisen's explanation of his condensation requires some modification. The figures in the above table show that the action of sodium on camphor is by no means complete, but it may be represented as follows:

(1.) $2C_8H_{14}\begin{cases}CH_2\\ |\\ CO\end{cases} + 2Na \rightarrow$

$$C_8H_{14}\begin{cases}CH\\ \|\\ C.ONa\end{cases} + C_8H_{14}\begin{cases}CH_2\\ |\\ CH.ONa\end{cases}.$$

(Sodium camphor.) (Sodium borneol.)

(2.) $C_8H_{14}\begin{cases}CH\\ \|\\ C.ONa\end{cases} + C_2H_5O.CO.CO.OC_2H_5 \rightarrow$

$$C_2H_5O.CO.C\begin{cases}ONa\\ -OC_{10}H_{15}\\ OC_2H_5\end{cases}.$$

(3) $C_2H_5O.CO.C\begin{cases}ONa\\ -OC_{10}H_{15}\\ OC_2H_5\end{cases} + \begin{matrix}H_2C\\ |\\ OC\end{matrix}\!\!>C_8H_{14} \rightarrow$

$$C_2H_5O.CO.CONa{:}C\begin{matrix}OC\\ |\\ \end{matrix}\!\!>C_8H_{14} + C_{10}H_{16}O + C_2H_6O.$$

The sodium salt when acidified yields the ketone directly.

[1] J. Thiele: *Ber. d. chem. Ges.*, **34**, 69 (1901).

The large amount of acid produced and the conditions which have been shown to favor its formation, prove that this cannot be ascribed to hydrolysis of the ethyl salt, either while the borneol and excess of camphor are being extracted, or as the result of traces of moisture in the apparatus. The idea that the borneol and camphor mechanically retain ethyl salt sufficient to yield, by subsequent hydrolysis, the amount of acid actually obtained, is also not supported by the comparative experiments. With the modifications already suggested, Brömme & Claisen's explanation of the formation of acetophenone oxalic acid may be accepted.[1] According to this the compound formed, as represented in the second equation, combines either with a second molecule of sodium camphor, or with one of sodium ethoxide, this last being produced from the alcohol eliminated in the third phase of the reaction:

(4). $C_{10}H_{15}O(NaO)(C_2H_5O)C.CO.OC_2H_5 + RONa \rightarrow$

$C_{10}H_{15}O(NaO)C.C(ONa)(OC_2H_5)(OR)$.

By the interaction of camphor as in equation 3, we get the salt $C_{10}H_{14}O:CONa.C(ONa)(OC_2H_5)(OR)$, which, with water, yields the compound $C_{10}H_{14}O:CONa.CO.ONa + C_2H_6O + ROH$ ($R = C_2H_5$ or $C_{10}H_{15}$). It must be confessed that this explanation is not wholly satisfactory, as it affords no very obvious reason for the failure of the ortho carbon atom in the above compound $C_{10}H_{14}O:C.ONa.C(ONa)(OC_2H_5)(OR)$, to react with camphor like the first one in equation 3, and yield, eventually, dicamphoroxalyl, $C_{10}H_{14}O:COH.COH:OC_{10}H_{14}$. Hitherto, none of this substance has been found, although attempts have been made to prepare it; therefore, the inference is, either that it is hydrolyzed during the extraction of the acid, or that the experimental conditions are

[1] *Ber. d. chem. Ges.*, **21**, 1132.

unfavorable for its production. A similar lack of success was experienced in an attempt to obtain the corresponding acetone derivative from ethyl camphoroxalate and acetone in the presence of sodium. An attempt which was made to test the above theory was based upon the following considerations: The symmetry of ethyl oxalate precludes the formation of more than one camphoroxalic acid, apart from possible stereoisomers, but an unsymmetrical dibasic ester should yield two structurally different acids according to which of the original carbethoxyl groups reacted; this is illustrated by the following equations, in which the carbon atoms of the carbethoxyl groups are distinguished as 1 and 2; ($R = C_2H_5$ or $C_{10}H_{15}$; $R'' = C_8H_{14} : CO$).

The additive compound $NaO.\overset{1}{C}(OR)_2 \cdots \overset{2}{C}(OR)_2.ONa$ of equation 4 would become successively

(*a*) $NaO.\overset{1}{C}:CR'' \cdots \overset{2}{C}(OR)_2.ONa$ or $NaO.\overset{1}{C}(OR)_2 \cdots \overset{2}{C}.ONa : CR''$;

(*b*) $NaO.\overset{1}{C} : CR'' \cdots \overset{2}{C} : O.ONa$ or $NaO.\overset{1}{C}O \cdots \overset{2}{C}.ONa : CR''$;

(*c*) $HO.\overset{1}{C} : CR'' \cdots \overset{2}{C}O.OH$ or $HO.\overset{1}{C}O \cdots \overset{2}{C}.OH : CR''$.

Pyrotartaric acid, $HO.OC.CH(CH_3).CH_2.CO.OH$, is perhaps the simplest acid fulfilling the conditions necessary to test the above hypothesis, and experiments were made with it. *Diethyl pyrotartrate* is readily prepared by E. Fischer's method, and the yield is excellent. Sodium wire dissolves slowly in a light petroleum solution of camphor and ethyl pyrotartrate; the condensation product which was finally isolated, gave a red coloration with ferric chloride and alcohol, but no acid could be obtained from it by hydrolysis. The yield of condensation product was small, and was not improved by the varying conditions employed. In pursuit of the same object *ethyl oxalacetate* was employed instead of the ethyl pyrotartate. The product was a syrup having a yellowish brown color in ethereal solution; in aqueous solution, a blue-purple coloration is produced on the addition of a little mineral acid; with a larger excess, the color is discharged; alkalies change it to deep red. When hydrolyzed, the compound yields a liquid acid which readily liberates carbonic anhydride from carbonates; an attempt to induce it to crystallize, after purification by means of the barium salt, was unsuccessful. The compound is probably a condensation product

of ethyl oxalacetate similar to those described by Claisen[1] alone, and in conjunction with Hare,[2] and by Ruhesmann and Hemmy.[3]

Camphoroxalic Acid is readily soluble in ether and benzene, moderately so in light petroleum, and sparingly in water ; it is preferably purified by recrystallization from light petroleum, being deposited in large, well-developed six-sided monoclinic plates, resembling those of quartz in appearance, and melting at 88°. When quickly distilled under the ordinary pressure some camphor is produced, but the greater portion of the acid passes over unchanged. Prolonged exposure to a temperature of 150° failed to yield any isomeric compound (cf. pp. 377). When heated with barium hydroxide, in a current of dry purified hydrogen, hydrolysis occurs at the position of the ethylene linkage, and camphor and barium oxalate are formed. No physiological action is produced on a dog by the intravenous injection of 0.241 gram of sodium camphoroxalate per kilo of body weight. The *copper, silver, calcium, lead, and barium salts* are sparingly soluble and amorphous ; the first is green, the second slightly yellow, and the remainder white. The *sodium salt*, which is very readily soluble, rapidly decolorizes potassium permanganate at the ordinary temperature. When reduced by means of sodium amalgam the acid yields a *lactone*, $C_8H_{14}\begin{cases}\text{CH.CH.OH.CO}\\ \quad\vert\qquad\quad\vert\\ \text{CH}_____\text{O}\end{cases}$, which is deposited from ether as an unctuous solid, melting at 75°–76°. The action of *bromine* on camphoroxalic acid was studied in the hope that it might yield evidence of the presence or otherwise of an ethylene linkage, and also because, by its means, it appeared possible that an isomeric acid might be produced. The substances react either in chloroform solution, or when bromine vapor is brought into contact with the dry acid ; hydrogen bromide is eliminated more quickly in the former than in the latter case, and the product is an oil which crystallizes with difficulty, cannot be completely purified, and contains bromine. It gives no coloration with ferric chloride and alcohol, and when reduced with magnesium amalgam yields an acid closely resembling camphoroxalic acid in general properties but differing from it in crystallographic form. These results may be explained in one of two

[1] *Ber. d. chem. Ges.*, **24**, 130.
[2] *Ibid.*, **24**, 120.
[3] *J. Chem. Soc.*, **71**, 334 (1897).

ways: If the ethylene linkage is attacked, the additive compound would be $C_8H_{14}\begin{cases}CBr.CBr.OH.CO.OH\\ |\\ CO\end{cases}$; this should readily eliminate hydrogen bromide and yields either the compound $C_8H_{14}\begin{cases}CBr.CO.CO.OH\\ |\\ CO\end{cases}$, or $C_8H_{14}\begin{cases}C:COBr.CO.OH\\ |\\ CO\end{cases}$; on reduction the former would give the diketonic acid,

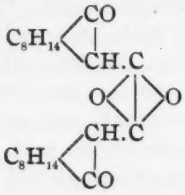
$$C_8H_{14}\begin{cases}CH.CO.CO.OH\\ |\\ CO\end{cases},$$

and the latter camphoroxalic acid. On the other hand it is well-known that camphor itself very readily combines with bromine, forming the dibromide $C_{10}H_{16}Br_2O$, which easily eliminates hydrogen bromide and is converted into bromocamphor, $C_{10}H_{15}BrO$; if the nucleus of camphoroxalic acid acts in a similar manner, then, by the reduction of this bromo acid, an isomeric camphoroxalic acid should be formed which should not differ materially from the ordinary compound in properties, and should give a similar red coloration with ferric chloride, while the keto acid could not do so. This second view of the reaction appears at present to be the more probable.

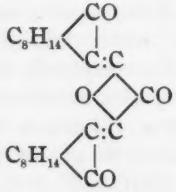
When heated with hydrochloric acid, or with dilute sulphuric acid (1 : 3), camphoroxalic acid yields a little oxalic acid, but by far the larger proportion of it is converted, by the addition of the elements of 2 mols. water, into an *acid* which crystallizes with some difficulty in granular nodules melting at 92°–93°. This compound, $C_{12}H_{20}O_6$, differs from the parent substance by its sparing solubility in light petroleum, the production of a deep blue coloration with ferric chloride and alcohol, and by its failure to give a precipitate with calcium chloride in ammoniacal solution.

The action of acetic anhydride on camphoroxalic acid is complex, and although much time and labor have been spent on its study, the results cannot be considered satisfactory. This arises from the fact that under the most favorable circumstances the yields are poor, and very slight alterations in the experimental conditions cause the acid to undergo complete decomposition. The purity of the anhydride employed is a most important factor. Three compounds have been isolated, the first is *acetylcamphor-*

oxalic acid, $C_8H_{14}\begin{cases}C:C(O.CO.CH_3).CO.OH\\ |\\ CO\end{cases}$, which is also formed by the interaction of the anhydride and ethyl camphoroxalate; it crystallizes from a mixture of benzene and light petroleum in reticulated stellate needles, melting at 133.5°–134.5°. The second compound is also formed by the action of benzoyl chloride on camphoroxalic acid; it gives no coloration with alcohol and ferric chloride, is insoluble in sodium hydroxide solution, and crystallizes in colorless slender needles melting at 192°–193°. Bromine and hydroxylamine are both without action on the compound to which the formula



is, at least provisionally, assigned. The third compound is formed with great difficulty, and all attempts to improve the yield were fruitless. It crystallizes in small, slender, colorless needles which darken at about 240°, and melt at 242°. It does not react with bromine in chloroform solution, while aqueous sodium hydroxide dissolves a portion and turns the remainder yellow. The formula



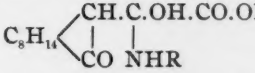
is in harmony with the little which is known of the substance.

Acetylcamphoroxalic acid readily reacts with bromine either in the form of vapor, or in chloroform solution; in both cases hydrogen bromide is copiously evolved, but no crystalline product could be isolated. The result confirms the explanation offered above of the action of bromine on camphoroxalic acid itself, and there appears little room for doubt that the haloid attacks the camphor nucleus of both compounds.

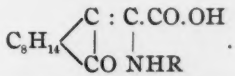
With benzoic anhydride, and camphoroxalic acid, no definite results could be obtained; at 110° benzoic acid sublimed, and at 150° carbonic anhydride was evolved.

Phenylhydrazine and camphoroxalic acid, in anhydrous ethereal solution, yield a salt which crystallizes in minute colorless needles, darkens at 205°, and melts and evolves gas at 214°–215°.

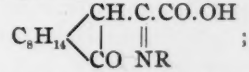
A somewhat extensive study has been made of the condensation compounds of camphoroxalic acid and amines, both of the aromatic and aliphatic series. The primary products in all cases are apparently simply additive substances of the type



but only one body of this formula has been isolated, that obtained from hydroxylamine: the remainder appear to be unstable, and eliminate the elements of water, giving rise to products of the general formula



Compounds of this nature have been prepared from ammonia, semicarbazine,[1] aniline, and α- and β-naphthylamine. These substances may then undergo further change; in the case of the aniline derivative carbonic anhydride is evolved; the hydroxylamine compound, mentioned above, loses the elements of two molecules of water and yields an isoxazole, while orthophenylenediamine condenses directly with the acid to form a quinoxaline derivative. The above series of compounds might be formulated in various other ways; perhaps one of the most plausible is

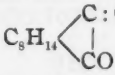


the three chief reasons for preferring the first formula are: (1) The stability of the compounds toward alkalies; (2) The fact that with all reagents that have been successfully tried, and which could afford crucial tests, both camphoroxalic acid, and ethyl camphoroxalate act as hydroxy-unsaturated compounds; hence, analogy is strongly in favor of adopting the same view in any

[1] It appears preferable to the writer to designate the compound $NH_2.CO.NH.NH_2$, *semicarbazine*, in analogy with phenylhydrazine.

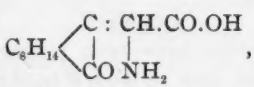
doubtful cases; (3) There is some direct evidence of the existence, in the above compounds, of the imido group, and in the case of the ammonium derivative, of the amido radical. On the other hand, there has been complete failure to obtain similar derivatives of secondary amines, either aliphatic or aromatic, and, except on stereochemical grounds, this is not readily explicable by the first formula, but is easily understood from the second one. It is hoped that subsequently further light may be obtained on the subject.

In naming the compounds the simplest and most advisable plan appeared to be to regard them as derived from the complex



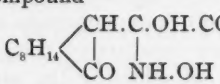
for which the term *camphoformene* suggests itself; it is self-explanatory and indicates the presence of the double linkage.

By the action of ammonia on sodium or potassium camphoroxalate, in alcoholic solution, at 100° under pressure, *sodium camphoformeneamine carboxylate* is obtained, from which the free *acid*,



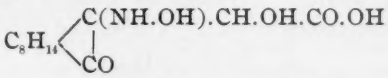
is readily liberated. It crystallizes in colorless plates, melts, and evolves gas at 178°, is not soluble in light petroleum, and gives no coloration with ferric chloride and alcohol. The acid dissolves readily in hot, but not in cold, sodium carbonate solution, and is reprecipitated on acidification ; by means of the diazo reaction it regenerates camphoroxalic acid. An attempt to prepare camphoformeneamine by heating the acid was unsuccessful ; absolute alcoholic ammonia and free camphoroxalic acid yield, as chief product, ammonium camphoroxalate, which is crystalline, and melts and evolves gas at about 212°.

Sodium camphoroxalate combines with hydroxylamine in concentrated aqueous-alcoholic solution, at the ordinary temperature, forming the compound

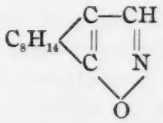


This crystallizes in bushy clusters of colorless, lustrous needles, which sometimes appear flattened into plates; it melts and

evolves gas at 146.5°. No alkaline fumes are evolved when the compound is boiled with sodium hydroxide solution, and no coloration is produced with alcohol and ferric chloride. That this additive compound is represented by the above formula, and not by the possible alternative one,



is proved by the production of *camphylisoxazole*,



when the additive compound is treated with a mixture of glacial acetic acid and acetic anhydride. The isoxazole crystallizes in colorless, lustrous needles, which melt at 124°–125°. At about 70° it sublimes slowly, and forms very slender, silky, long needles; no coloration is produced with concentrated nitric acid.

Semicarbazine combines with camphoroxalic acid under the same conditions as hydroxylamine, and also in alcoholic solution, under pressure, at 100°. The product consists of two compounds which are separated by means of ether. The more soluble one crystallizes from acetone in small white needles, melting and decomposing at 218°. The second compound is insoluble in all ordinary neutral organic media; it is purified by means of glacial acetic acid and alcohol, and is deposited in microscopic needles—aggregated into cubical clusters; these melt and decompose at 209°–210°. Both compounds dissolve in sodium carbonate solution with equal readiness; the first is reprecipitated in a gelatinous condition, but after drying, its melting-point is unchanged. The solution of the second compound is also precipitated by acids, but the precipitate shows the same melting-point as the "soluble" body. Identical results are obtained by the elementary analysis of the two substances. It would be easy to suggest possible explanations of the above phenomena, but it appears better to abstain from doing so until more experimental information is forthcoming.

Aniline and camphoroxalic acid yield three compounds, one of these, *phenylcamphoformeneamine carboxylic acid*,

$$C_8H_{14}\begin{cases} C : C.CO.OH \\ | \quad | \\ CO\ NH.C_6H_5 \end{cases},$$

corresponds with the ammonia derivative of camphoroxalic acid, and is formed by boiling aniline with sodium camphoroxalate in aqueous alcoholic solution; it crystallizes in bright yellow needles, and melts and decomposes at 174°. The second compound,

$$C_8H_{14}\begin{cases} C : C.CO.ONH_3C_6H_5 \\ | \quad | \\ CO\ NH.C_6H_5 \end{cases},$$

is the *aniline salt* of the preceding acid, and is formed by warming for a few moments on the water-bath, a mixture of aniline and camphoroxalic acid in concentrated benzene solution. It crystallizes from benzene on the addition of light petroleum, in small, colorless needles which melt and decompose at 158°. The salt is stable at the ordinary temperature in the absence of moisture and acid vapors; when cautiously heated below its melting-point, it is resolved into aniline and phenylcamphoformeneamine carboxylic acid, and the same change is produced immediately by dilute sulphuric acid, hydrochloric acid, alkalies, and more slowly, by water. Rapid heating above its melting-point results in the production of aniline, carbonic anhydride, and phenylcamphoformeneamine (see below). Prolonged boiling with concentrated alkali, aqueous or alcoholic, converts the carboxylic acid, and therefore, of course, the aniline salt, into aniline and the alkali salt of camphoroxalic acid.

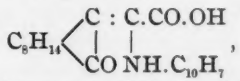
The third compound from aniline and camphoroxalic acid is formed by heating either of the preceding substances above their melting-points, and also by the direct action of the constituents at 130°. Its preparation and reactions characterize it as *phenylcamphoformeneamine*,

$$C_8H_{14}\begin{cases} C : CH \\ | \quad | \\ CO\ NH.C_6H_5 \end{cases}.$$

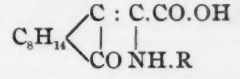
It crystallizes in colorless, rhombic plates, and occasionally in characteristic slender hair-like needles, upwards of an inch in length. With bromine, it forms a *hydrobromide*, while hydroaurochloric acid and hydroplatinochloric acid yield *salts*, of which the former is very unstable. Prolonged boiling with concentrated alkali is without effect on the compound. With acetic anhydride an unstable crystalline derivative is obtained which melts at 134°.

Benzoyl chloride reacts with the amine, yielding crystals resembling those of potassium nitrate in shape, and melting at 160–161°. The derivative formed by the action of phenylsulphonic chloride is crystalline, melts at 133°, and does not dissolve in sodium hydroxide solution. With methyl iodide, the amine apparently does not react.

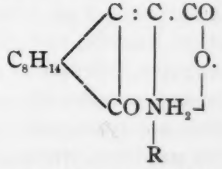
α-Naphthylamine reacts with sodium camphoroxalate under somewhat similar conditions to aniline and forms *α-naphthylcamphoformeneamine carboxylic acid*,



which crystallizes with ½ mol. C_6H_6 in well developed, transparent, amber-colored prisms, melting at 170°. At a little above 100°, the crystals lose their benzene and change to a brown powder which also melts at 170°. The corresponding *derivative* of *β-naphthylamine* is deposited from benzene or toluene in bright yellow needles which melt and decompose at 173°. From neither of these compounds has it hitherto been possible to obtain a naphthyl camphoformeneamine, corresponding with the phenyl-derivative. The pronounced color—bright yellow to brown,—of these three carboxylic acids suggests the possibility, that instead of being represented by the formula

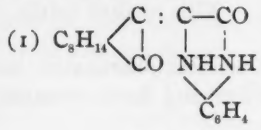


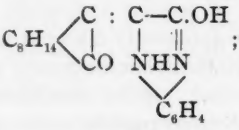
they, in reality, possess a "betaine" structure,

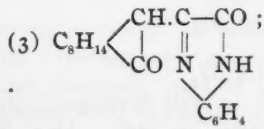


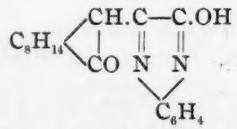
The interaction of orthophenylenediamine and camphoroxalic acid, carried out under similar conditions to those employed for the preparation of the preceding carboxylic acids, results in the production of *camphoquinoxaline*, $C_{18}H_{20}N_2O_2$; it crystallizes in bright yellow needles, melts at 246°, and dissolves in concentrated sulphuric acid, giving a color resembling that produced by potassium chromate in the same circumstances. Under conditions

which preclude the idea of hydrolysis, ethylic camphoroxalate and orthophenylenediamine yield a substance identical with that from the acid. The compound may be represented by one or other of the formulae:









The relationship of formulae 1 and 2 to 3 and 4 respectively, is that of a lactam to the corresponding lactim; excluding this aspect of the question as involving the broader one of the constitution of the quinoxalines, sodium camphoroxalate should give the compound having the second formulae, while ethylic camphoroxalate should yield that represented by the first one. Hence it must be concluded, either that the first compound is unstable and changes spontaneously into the second, or that the sodium salt of the second, after acidification, changes to the first; at present, this latter suggestion appears to be the more probable, unless, of course, the case is one of tautomerism in the strict sense of the term.

ETHYL CAMPHOROXALATE.

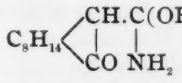
The crude condensation product of ethyl oxalate and camphor always contains ethyl oxalate, and although this is of little consequence for some purposes, a supply of pure substance is, of course, highly desirable and occasionally absolutely necessary. The crude ethyl salt does not react with copper acetate either in neutral, or ammoniacal solutions, irrespective of whether the ester is dissolved in water, ether, or light petroleum. The compound thus exhibits a striking contrast to formylcamphor, which is a strong acid. When boiled, a portion suffers decomposition and part is volatilized unchanged. An attempt to separate the mixed ethyl salts by systematic treatment with sodium hydroxide, sodium carbonate, and sodium hydrogen carbonate solutions, resulted only in the hydrolysis of the compounds. It

was ultimately found to be most convenient to hydrolyze the crude ester, and then esterify the purified camphoroxalic acid by a modification of E. Fischer's method. The compound is deposited from light petroleum in fern-like aggregates, consisting of long needles, melting at 40.5°. It is miscible with ether in all proportions, and is extremely readily soluble in ordinary media, with the exception of light petroleum. With alcohol and ferric chloride solution a deep red coloration is obtained. Fractional esterification failed to show any lack of homogeneity in camphoroxalic acid (cf. pp. 368).

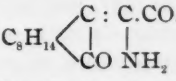
Bromine and ethylic camphoroxalate readily react, hydrogen bromide being evolved; when the two are heated in chloroform solution oxalic acid is formed, but at the ordinary temperature the product was an oil which refused to crystallize.

With acetic anhydride the ester yields acetylcamphoroxalic acid, as already described (cf. p. 369). No derivative could be obtained by the action of either benzoyl chloride or benzoic anhydride, in spite of considerable variation of the experimental conditions. The greater relative stability of the ethylic salt, as compared with camphoroxalic acid, towards these reagents, is interesting, and supports the view that the acid, under their influence, undergoes deep-seated changes involving the carboxyl group.

Carefully dried ammonia produces a white precipitate when passed into a well cooled absolute alcoholic solution of ethylic camphoroxalate; the substance is unstable, and is resolved spontaneously into its constituents. It is doubtless an additive compound with the formula



When heated at 100°, with alcoholic ammonia in excess, it is converted into *camphoformeneaminecarboxylamide*,

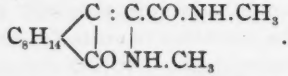


which is also formed directly by the interaction of ammonium chloride, potassium hydroxide, and ethylic camphoroxalate under the same conditions. It crystallizes in colorless microscopic needles, melting at 227°–228°. Boiling with sodium hydroxide solution causes the regeneration of ammonia and camphoroxalic acid.

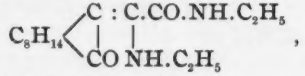
A compound which melted at 225°, and was previously[1] obtained by the action of dry ammonia on ethyl camphoroxalate in absolute ethereal solution, was prepared from the crude ethylic salt, containing, therefore, ethyl oxalate, and was almost certainly oxamide.

In the first paper on this subject,[2] a substance was described which was produced by the interaction of crude ethyl camphoroxalate and hydroxylamine; it crystallized in silky needles, and melted at 193°. From its melting-point and general properties, the compound is probably oxalenediamidoxime $OH.N:C(NH_2).C(NH_2):N.OH$; in any case it is not a derivative of ethyl camphoroxalate, as all attempts to obtain it from the pure compound were fruitless. Experiments with the ethyl salt and hydroxylamine at 100° led to no definite results, but at the ordinary temperature a product is formed which crystallizes in colorless, slender needles, melting at 120°–121°. Its nature has not yet been investigated.

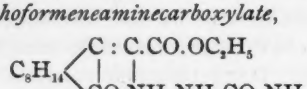
Methylamine and ethyl camphoroxalate readily condense at 100°, under conditions similar to those employed in the case of ammonia. The product is deposited in small, white needles which melt at 130°; it is not very stable, and spontaneously evolves methylamine, but there is no doubt that it is *methyl camphoformeneaminecarboxylmethylamide*,



Ethyl camphoformeneaminecarboxylethylamide,



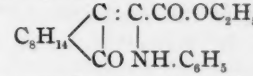
is formed from ethylamine in a similar manner to the preceding compound, which it resembles in general properties; it crystallizes in colorless needles, melts at 148°, and very slowly evolves ethylamine. Semicarbazine condenses with ethyl camphoroxalate, either at the ordinary temperature, or at 100°, forming *ethyl semicarbazylcamphoformeneaminecarboxylate*,



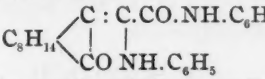
[1] *Am. Chem. J.*, **20**, 332 (1898).
[2] *J. Chem. Soc.* (London), **57**, 655 (1890).

which crystallizes in colorless needles, melting at 202°. Molecular weight determinations agree with the formula given. Accompanying this compound a second was sometimes obtained in small quantity which also crystallized in colorless needles, melted at 225°, and may possibly be semicarbazine sulphate.

Ethyl camphoroxalate forms two compounds with aniline. The one, *ethyl phenylcamphoformenecarboxylate*,

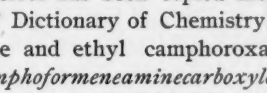


is prepared from its constituents, at 100°, and is deposited in almost white, microscopic, needle-shaped crystals, melting and decomposing at 158°–160°. When hydrolyzed by means of alkalies it yields the corresponding *acid*, m. p. 174, the preparation of which from aniline and sodium camphoroxalate has been already described (cf. p. 374). The second condensation product of aniline and ethyl camphoroxalate is obtained by heating these substances together at 130°; it consists of *phenylcamphoformeneaminecarboxylicanilide*,



which crystallizes in small, colorless needles, melting at 193°. The compound is not changed by admixture with bromine in chloroform solution, nor by prolonged boiling with aqueous or alcoholic sodium hydroxide. Treatment with sulphuric acid readily gives rise to resinous products. An unstable *platinochloride* appears to be formed, but hydroaurochloric acid quickly undergoes reduction when mixed with the anilide. In the first paper on this subject it was stated that aniline and ethyl camphoroxalate yield oxanilide; this is incorrect as the foregoing account shows. At the time that the statement was made pure ethyl camphoroxalate had not been prepared, and the mistake arose from the use of crude material containing ethyl oxalate. Unfortunately the error has been copied into Morley & Muir's edition of "Watts' Dictionary of Chemistry."

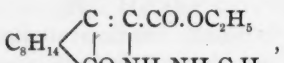
β-Naphthylamine and ethyl camphoroxalate yield, at 100°, *ethyl β-naphthylcamphoformeneaminecarboxylate*,



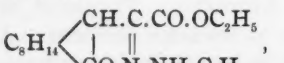
which closely resembles the corresponding phenyl derivative in appearance, and crystallizes in colorless, microscopic needles, softening at about 160°, and melting and decomposing at 174°. The exact melting-point is largely dependent on the rapidity with which the bath is heated. Hitherto, no naphthalide has been obtained corresponding to the "anilide" described above.

The condensation of orthophenylenediamine and ethyl camphoroxalate, leading to the production of camphoquinoxaline, has been described in connection with camphoroxalic acid (p. 375).

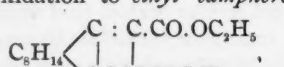
Phenylhydrazine and ethyl camphoroxalate, in equimolecular proportion, readily react when boiled in anhydrous ethereal, or light petroleum solution. The product is sparingly soluble, and comparatively stable towards aqueous sodium hydroxide at the ordinary temperature, but gives a deep blue-purple coloration with concentrated nitric acid. It crystallizes in slender, small, white needles, which melt sharply at 212°. A trace of impurity depresses this value very considerably; hence the incorrect melting-point (187°–188°) given in the first paper. The proof that this compound is a *phenylhydrazide*,



and not a *phenylhydrazone*,

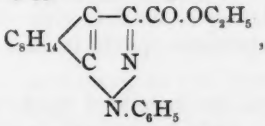


is afforded by its oxidation to *ethyl camphoroxalateazobenzene*,

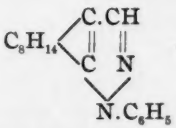


which crystallizes in red needles, melts at 210°, and is much more readily soluble in ether than the phenylhydrazide. The oxidation may be accomplished by means of mercuric oxide in the presence of absolute alcohol, but is preferably carried out by the help of hydrogen peroxide at the ordinary temperature in ethereal solution. The proof of the constitution of this compound affords a strong argument, by analogy, in favor of that assigned to the other condensation compounds described in the preceding pages.

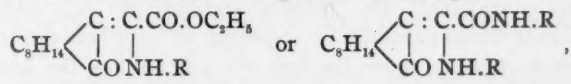
Ethyl camphylphenylpyrazolcarboxylate,



is formed by heating the phenylhydrazide at 200°, or by treating it with acetic anhydride, glacial acetic acid, or hydrogen chloride. It crystallizes in bunches of white needles, melts at 114°, and gives a pale yellow-colored solution with concentrated nitric acid. The free *acid*, prepared by hydrolyzing the preceding compound, crystallizes in lustrous needles, which melt at 192°; these appear to contain benzene of crystallization, as they slowly lose their luster, even at the ordinary temperature, and then melt at 197°. The compound, in the form of *sodium salt*, is without marked physiological action. When the *barium salt* is distilled with excess of barium oxide, care being taken to avoid the presence of moisture, an oily compound is formed which gives a reddish purple coloration with concentrated nitric acid, and also Knorr's pyrazoline reaction; it therefore, presumably, contains *camphylphenylpyrazole*,



The study of the preceding condensation compounds shows that their stability increases as the mass of the radical in the amine becomes greater, at least as regards the aliphatic derivatives; in the case of ammonia the symmetry of the molecule probably accounts for the high melting-point of the product. The question as to the formation of compounds of the type,



appears to depend upon the basicity of the amine, and the temperature at which the reaction proceeds; thus at 100°, when R = H, CH_3, or C_2H_5, compounds of the second type are obtained, but when R = NH.NH.CO.NH_2, C_6H_5, NH, C_6H_5, or $C_{10}H_7$, the products belong to the first type. At higher temperatures, with R = C_6H_5, a compound of the second type is produced, but under

similar conditions, when R = $C_{10}H_7$, this was not found to be the case. The substances of the first type are strict analogues of the primary condensation products of camphoroxalic acid and amines.

It is worthy of note, that in spite of many attempts to prepare them, no compounds could be isolated in which the carbonyl group of the camphor nucleus had primarily reacted with an amine; that it had remained intact was proved by the subsequent formation, from the actual condensation-products of pyrazole, and isoxazole derivatives. It is now generally recognized that many α-β, α-γ, and α-Δ-diketones are capable of existing or reacting in two or more forms, the change may be expressed by the equation: CHR.CO$\rightleftarrows$CR:C.OH. Analogy leads to the conclusion that all compounds of these classes are capable, under suitable conditions of undergoing the change. It is customary to assume that the ordinary "ketonic reagents" react primarily with the carbonyl group, giving compounds of the type of aldehyde ammmonia

$$CHR.C\begin{matrix}NH_2\\OH\end{matrix},$$

which are generally unstable and change spontaneously into CHR.C:NH(R)+H_2O (formation of oximes, hydrazones, etc.). This idea of the carbonyl group, *always* being the point of attack, does not appear to have any very definite foundation. The above results show that "ketonic reagents," in the presence of a compound containing both carbonyl and the group R_2C:C.OHR, react preferably with the latter, and not at all with the former under any conditions hitherto devised, and that, in the case of hydroxylamine, the compound formed by its addition to the double carbon linkage is quite stable. Similar results were subsequently obtained with mesityl oxide and phorone by Harries and his coworkers.[1] The relative stability of such additive compounds would naturally be expected to vary between limits at least as wide as those limiting the existence of the ketonic and enolic forms of the parent substances. Moreover, the stability might be greatly dependent on the reagents with which the compounds are brought into contact. In cases where the group in question could occur twice or thrice, as in triketones, such as

$$R.CO.CH_2.CO.CH_2.CO.R',$$

[1] Ber. d. chem. Ges., 30, 231, 2726 (1897).

the forms,

$$R.COH:CH.CO.CH_2.CO.R'$$

and

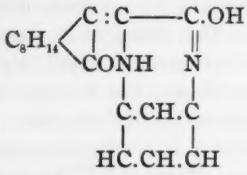
$$R.COH:CH.COH:CH.CO.R,$$

might be produced successively as any given reaction proceeded, the end products being, of course, direct derivatives of these forms and not the free enolic bodies themselves. On the other hand, the production of the enolic form might, at any given stage of the reaction, be entirely inhibited by the chemical or stereometrical influence of the new groups which become linked to the original molecule. In the preceding sentences, the ketonic and enolic forms of ketones have been referred to, for the sake of simplicity, as if they were fixed quantities; in reality we should doubtless regard them as extreme phases of reversible systems, tending, with very varying velocities, towards more or less widely separated states of equilibrium. The question naturally arises whether the above considerations are not also applicable to monoketones; in this connection, Freer's very interesting researches on acetone may be mentioned; they show that under certain conditions it forms derivatives of the compound $CH_3.COH:CH_2$. An attempt has been made to discover whether any simple relationship exists which would explain the production of highly colored ferric compounds by the enolic forms of diketones and of phenols, but so far, unsuccessfully.

Whatever may be the fate of these suggestions, some explanation must ultimately be given of the following facts: (1) The great reactivity of the "carbonyl" group in camphor with a number of reagents which are generally regarded as tests for the presence of this radical; (2) of the complete quiescence of this group in camphoroxalic acid towards the same reagents; (3) of the great reactivity of the second "carbonyl" in that acid; (4) of the fact that this last group certainly reacts as an unsaturated hydroxyl complex towards some of the reagents, and possibly does so with them all.

Condensation products could not be obtained from ethyl camphoroxalate or sodium camphoroxalate, with the amines enumerated below, under the conditions employed in the preparation of the compounds described in the preceding pages. For convenience both classes of failures are discussed together. *Urea*, *para-* and *meta-phenylenediamine*, *ethylaniline*, and *dimethylaniline*

failed to react with either ethyl or sodium camphoroxalate; *α-naphthylamine* reacted with the latter but not with the former; *dimethylamine* was only tried with the ethyl salt, with which it did not combine. The failure in the case of urea is probably due to its comparatively feeble basicity, while that with meta- and para-phenylenediamine is ascribable to the difficulty of producing rings of seven and eight members, such as



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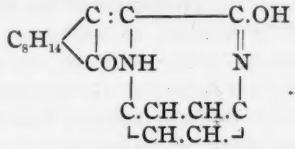
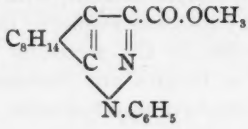


The behavior of secondary amines (ethylaniline and dimethylamine) has already been discussed (cf. p. 372), and dimethylaniline, being a tertiary base, would not be expected to react. For the failure of α-naphthylamine to condense with ethyl camphoroxalate, while it interacts so readily with sodium camphoroxalate, no very plausible reason can, at present, be suggested.

Ethyl camphoroxalate readily combines with methyl iodide, in the presence of silver oxide, forming *ethyl methylcamphoroxalate* which appears to be an oil; the corresponding *acid* crystallizes in six-sided prisms and plates, and melts at 95°–96°. Like the ethyl salt it gives no coloration with ferric chloride and alcohol.

Methyl oxalate condenses with camphor, in presence of sodium methoxide, but the time of heating requires to be prolonged owing to the sparing solubility of the resulting sodium salt in light petroleum. It is, therefore, more readily prepared by esterifying the acid. The *compound* crystallizes from light petroleum in arborescent needles, belonging to the orthorhombic system, which melt at 74.5°–75°. With phenylhydrazine, methyl camphoroxalate yields a *phenylhydrazide*, which is deposited from methyl alcohol in slender, white needles, melting at 204°–205°. *Methyl camphylphenylpyrazolecarboxylate*,



is formed by the interaction of the phenylhydrazide and glacial acetic acid. It crystallizes in colorless needles, melts at 80.5°–81.5°, and when hydrolyzed yields the acid (m. p. 193°–194°) described above (p. 381).

The preparation of *isoamyl camphoroxalate* was necessarily preceded by that of isoamyl oxalate. The only method described in Beilstein's "Handbuch" is due to Friedel and Crafts, and consists in heating ethyl oxalate with isoamyl alcohol at 220°–250°. No difficulty was experienced in obtaining the compound, in any desired quantity, by the action of isoamyl alcohol on dehydrated oxalic acid at 100°. The preparation of *isoamyl camphoroxalate* was carried out in a similar manner to that of the ethyl salt. The sodium dissolves easily, and the resulting compound is readily soluble in light petroleum. The isoamyl salt itself is sparingly soluble in ether, and crystallizes in colorless triclinic needles, melting at 98.5°–99.5°. The chief object in view in preparing this compound was to ascertain the influence, if any, of the increase of the mass of the carbalkyloxy group on the course of the condensation. The results show that it proceeds more readily with the higher than with the lower homologues; the solubility in ether or light petroleum of ethereal sodium salts also increases as the mass of the alkyl becomes greater, and it is highly probable that this is the chief reason, if not practically the only one, for the improved yield, as the sodium is more readily dissolved. On the other hand the solubility of the free ethereal salts in ether and light petroleum is least in the case of isoamyl, greatest in that of ethyl, while methyl occupies the intermediate position. As regards melting-points the compounds resemble the corresponding ethereal salts of oxalic acid since the ethyl derivative melts at a lower temperature than the methyl salt.

Isoamylic camphoroxalate phenylhydrazide, prepared in a similar manner to the lower homologues, is very sparingly soluble in ordinary media, with the exception of isoamyl alcohol, at the boiling-point of which it slowly suffers decomposition.

Condensation takes place tolerably readily between camphor and ethyl pyruvate; the product is difficult to purify and has, therefore, hitherto not been investigated.

EXPERIMENTAL.

Camphoroxalic Acid.

The best method of preparing this compound in quantity has been previously described.[1]

Ammonia and Camphoroxalic Acid.

The acid (4.4 grams = 1 mol.) was mixed in a bottle of about 150 cc. capacity, with ammonium chloride (3.2 grams = 3 mol.), potassium hydroxide (4.5 grams = 4 mol.) and alcohol (95 per cent., 50 cc.); the bottle was provided with a well fitting glass stopper which was suitably clamped, and the contents heated at 100° in a water-bath during four hours. When cold, the alcohol was removed by evaporation, and the residue treated with water, acidified with dilute sulphuric acid, and extracted three times with ether. The solid residue from the dried ethereal solution was then recrystallized several times from benzene, and finally from a mixture of acetone and light petroleum. The compound, which is *camphorformeneamine carboxylic acid*, is deposited in colorless plates melting at 178° with evolution of gas; it is readily soluble in benzene, acetone, and ethyl acetate, insoluble in light petroleum. It does not dissolve in sodium carbonate solution at the ordinary temperature, but does so readily when heated, and is reprecipitated on acidification. With alcohol and ferric chloride no coloration is produced, but a deep red one is obtained if the compound is previously treated with hydrochloric acid and potassium nitrite. Sodium hydroxide may be employed for the preparation of the compound instead of potassium hydroxide.

Analysis:

I. 0.2485 gram substance gave 0.5850 gram carbon dioxide and 0.1720 gram water.

II. 0.1946 gram substance gave 10 cc. nitrogen at 13° and 755 mm.

III. 0.1207 gram substance gave 6.8 cc. nitrogen at 28.5° and 741.5 mm.

	Calculated for $C_8H_{14}\langle^{C:C.CO.OH}_{CONH_2}$	Found.		
		I.	II.	III.
Carbon.....	64.57	64.20	....	....
Hydrogen.....	7.62	7.69	....	....
Nitrogen.....	6.28	....	6.04	6.01

When heated at 170°–180°, the compound evolves gas; the resinous residue dissolves in alcohol, and also in hydrochloric

[1] *Am. Chem. J.*, **19**, 399 (1897); **21**, 247 (1899).

acid; from this latter solution sodium hydroxide precipitates an amorphous substance, while platinic chloride gives crystals of ammonium platinichloride, which were identified by analysis and comparison with a pure preparation of that salt. It is thus evident that the attempt to eliminate the carboxyl group in this simple manner from the original compound was unsuccessful.

By the action of free camphoroxalic acid on absolute alcoholic ammonia, in excess, at 100°, under pressure, a crystalline compound is formed which melts and evolves gas at about 212°, but when very slowly heated it melts at about 100°. Ammonia is evolved when the compound is boiled with aqueous sodium hydroxide, and the solution, after acidification, gives a deep red coloration with ferric chloride and alcohol. The compound is presumably *ammonium camphoroxalate.*

ETHYL CAMPHOROXALATE DERIVATIVES.

Ammonia and Ethyl Camphoroxalate.—The ester (5 grams = 1 mol.) was mixed with ammonium chloride (3.2 grams = 3 mol.), potassium hydroxide (3.1 grams = less than 3 mol.), and alcohol of 95 per cent. (50 cc.). The mixture was then heated in a closed bottle, at 100°, during four hours. The alcohol was removed on the water-bath, the residue washed with water and dried. The yield is practically quantitative. The compound is sparingly soluble in chloroform, acetic acid, alcohol, and benzene, but readily in xylene; it was crystallized from this three times, and after being washed with benzene formed colorless, microscopic needles melting at 227°-228°.

Analysis:

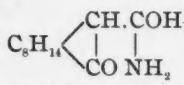
I. 0.2158 gram substance gave 0.5086 gram carbon dioxide.
II. 0.2135 gram substance gave 0.5040 gram carbon dioxide and 0.1560 water
III. 0.1274 gram substance gave 14.0 cc. nitrogen at 18.5° and 743 mm.
IV. 0.1323 gram substance gave 15.4 cc. nitrogen at 19.5° and 747 mm.
V. 0.2061 gram substance gave 23.4 cc. nitrogen at 17.5° and 750 mm.

	Calculated for $C_8H_{14}\begin{smallmatrix}C:C.CONH_2\\ \vert\ \ \vert\\ CONH_2\end{smallmatrix}$	Found.				
		I.	II.	III.	IV.	V.
Carbon.....	64.86	64.28	64.38	....	....	....
Hydrogen...	8.10	....	8.11	....	....	....
Nitrogen....	12.61	....	....	12.31	13.11	12.97

Camphoformeneaminecarboxylamide gives no coloration with ferric chloride and alcohol; when boiled with aqueous sodium

hydroxide, ammonia is evolved, and the residue, after acidifying, gives, on the addition of ferric chloride and alcohol, the deep red coloration characteristic of camphoroxalic acid. The amide is also produced by heating ethyl camphoroxalate, or the ammonia additive compound of this mentioned below, with alcoholic ammonia at 100° in a sealed tube ; the yield is excellent, but the method is not so convenient as the one given above. With alcoholic hydroplatinichloric acid the amide yields a sparingly soluble *platinichloride* which crystallizes in hexagonal, orange-colored plates.

A second compound of ammonia and ethylic camphoroxalate is obtained by saturating a concentrated, well cooled solution of the latter, in absolute alcohol or ether, with the anhydrous gas. A white precipitate is formed, which, when removed, and drained on a porous plate, is gradually resolved into its constitutents. The substance could not be analyzed, but is almost certainly the simple additive *compound*



When heated with alcoholic ammonia in a sealed tube at 100°, camphoformeneaminecarboxylamide is obtained as described above. A third *compound*, which has been previously described, was obtained by the action of dried ammonia on *crude* ethylic camphoroxalate in anhydrous ethereal solution; it darkens at about 200°, melts at 225°, and is possibly impure oxamide, as subsequent experiments with the purified ester failed to yield it.

Hydroxylamine and Ethyl Camphoroxalate.

The ester (1 mol.) is dissolved in alcohol and mixed with a concentrated, aqueous solution of hydroxylamine hydrochloride (3.5 mol.); more alcohol is added if necessary to obtain a clear solution, and then solid sodium hydrogen carbonate until the liquid is slightly alkaline. The mixture is allowed to remain at the ordinary temperature during six days, in the course of which a white granular precipitate gradually forms. The liquid is then poured into water, acidified with dilute sulphuric acid, and extracted three times with ether. The ethereal solution is dried and distilled, and the residue crystallized twice from a mixture of toluene and light petroleum ; it is deposited in colorless, slender needles melting at 120°–121°. The *compound* is readily soluble

in aqueous sodium hydroxide, more slowly in sodium carbonate solution; it dissolves in dilute sulphuric acid when heated, but crystallizes out on cooling. It does not appear to be soluble in water to any great extent, but when heated it melts and floats on the surface. An attempt to obtain the compound by the interaction of its constituents at 100°, under pressure, in the manner described in the preparation of camphoformeneaminecarboxylamide was not successful, neither did the ester react at all with hydroxylamine in absolute alcoholic solution, under pressure, at 100°. The constitution of this substance will be further investigated subsequently.

In the first paper on this subject (*loc. cit.*) brief mention was made of a *compound* obtained from *crude* ethylic camphoroxalate and hydroxylamine, as the latter was employed in the form of hydrochloride, and a large excess of potassium hydroxide added; it follows that the substance should be a derivative of a camphoroxalic acid and not of the ethyl salt. The body has now been further investigated, and it appears to be a *potassium salt* of an oxalic acid derivative; this is readily understood when it is remembered that the only specimens of ethyl camphoroxalate at that time procurable necessarily contained ethyl oxalate in varying proportion. The compound crystallizes in colorless, silky needles, melts at 193° with sudden decomposition, is readily soluble in water and sodium hydroxide solution, more sparingly in dilute alcohol, and is practically insoluble in absolute alcohol. It gives a red coloration with alcohol and ferric chloride after being boiled with hydrochloric acid, but oxalic acid could not be detected in the solution. The readiness with which it explodes, on heating, rendered the analysis so difficult that, after several unsuccessful attempts, further effort was abandoned.

Methylamine and Ethyl Camphoroxalate.—The ester (5 grams = 1 mol.) was mixed with methylamine hydrochloride (4 grams = 3 mol.), potassium hydroxide (3 grams = less than 3 mol.) and alcohol (95 per cent., 50 cc.) and heated under pressure, at 100°, during four hours. The alcohol was removed on the water-bath, the residue treated with water, and extracted with ether. The ethereal solution, after drying, was distilled. The crystalline residue consisted of *methyl camphoformeneaminecarboxylmethylamide;* it was purified by repeated crystallization from benzene, with the addition of light petroleum, and was deposited

in small, white needles, melting at 130°. The compound is less readily soluble in benzene than the ethyl derivative described below, and is somewhat unstable; on this account, and from the difficulty of completely freeing it from ash, which contained iron, its analysis was abandoned after several unsuccessful attempts had been made.

The aqueous liquid remaining after the removal of the amine was acidified with dilute sulphuric acid, and extracted with ether; this, after drying and distillation, gave only a small residue consisting, apparently, of impure camphoroxalic acid.

Ethylamine and Ethyl Camphoroxalate.—The experiments with ethylamine were carried out exactly as in the case of methylamine, the quantities of materials employed being ester (5 grams = 1 mol.), ethylamine hydrochloride (3.2 grams = 2 mol.), potassium hydroxide (2 grams = less than 2 mol.), and 95 per cent. alcohol, (50 cc.). The product, *ethyl camphoformeneaminecarboxylethylamide*, readily dissolves in ethyl acetate and benzene, but is insoluble in light petroleum. It gives no coloration with alcohol and ferric chloride solution, but even when purified, slowly evolves ethylamine. It is deposited from benzene, after two crystallizations, in colorless needles melting at 148°. The yield is good. The compound is also formed by the action of free ethylamine on the ester, in absolute alcoholic solution at 100°, under pressure.

Analysis:

I. 0.2606 gram substance gave 0.6558 gram carbon dioxide and 0.2262 gram water.

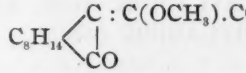
II. 0.1326 gram substance gave 11.8 cc. nitrogen at 18.5° and 739 mm.

	Calculated for $C_8H_{14}\langle^{C:C.CONH.C_2H_5}_{CONH.C_2H_5}$	Found. I.	Found. II.
Carbon	69.06	68.63	..
Hydrogen	9.35	9.64	..
Nitrogen	10.07	..	9.96

Ethyl Camphoroxalate and Methyl Iodide.—The ethyl salt (2.5 grams) was mixed with dried silver oxide (3.5 grams),[1] and methyl iodide (3 grams), and heated in a sealed tube, at 100°, during four hours. The product was filtered, the silver compounds repeatedly washed with ether, and the combined filtrate and washings allowed to evaporate. The residue did not crystallize. It consisted of *ethyl methylcamphoroxalate* as it gave

[1] Cf. Lauder: *J. Chem. Soc.* (London), **77**, 729 (1900).

no coloration with alcohol and ferric chloride. The corresponding *acid*,



was obtained by hydrolyzing the preceding compound with dilute aqueous-alcoholic sodium hydroxide at 100°. It readily crystallizes from light petroleum in large hexagonal-shaped prisms and plates, and melts at 95°–96°. It gives no coloration with alcohol and ferric chloride, but with ammonium hydroxide and calcium chloride it gives a white precipitate soluble in acetic acid, thus resembling camphoroxalic acid. It is apparently gradually converted into this acid on exposure to the air.

Ethyl Camphoroxalate and Acetone.—These two compounds do not appear to react when mixed and treated with sodium in equimolecular proportion, in the presence of light petroleum. Some of the metal immediately dissolves, but the remainder is not attacked after boiling during two hours. Sufficient absolute alcohol was added to combine with the sodium, but the only product which could be eventually isolated was camphoroxalic acid. The similar negative result was obtained with *ethyl camphoroxalate and camphor*, the experiments being carried out under similar conditions to those just described.

Ethyl Pyruvate.—This compound can be readily prepared by the method of esterfication previously described (*loc. cit.*). Pyruvic acid (50 grams) is mixed with 95 per cent. alcohol (500 cc.), and conc. sulphuric acid (80 cc.) and boiled during seven hours. The excess of alcohol is removed on the water-bath, the acid being simultaneously neutralized with sodium hydrogen carbonate, the product poured into water, extracted with ether, and the ethereal solution washed, if needful, with sodium hydrogen carbonate solution.

Ethyl Pyruvate and Camphor.—When treated with camphor, (1 mol.) and sodium wire (1.5 atoms), in light petroleum solution, condensation apparently takes place. The product has hitherto proved difficult to purify; it gives a deep red coloration with ferric chloride and alcohol.

The work will be continued and extended in various directions as time permits.

LEWIS INSTITUTE, CHICAGO, ILL.

SYNTHESIS OF DERIVATIVES OF DIMETHYLCYCLOPENTANONE, $\beta\beta$-DIMETHYLADIPIC ACID, AND $\alpha\beta\beta$-TRIMETHYLADIPIC ACID.[1]

By W. A. Noyes.

Received April 29, 1901.

SOME time since, the author reported on the synthesis of 2.33-trimethylcyclopentanone,[2] and its identification with a ketone previously obtained from camphoric acid by a series of easily interpreted reactions. As the study of this ketone and of related compounds, seems likely to prove of some importance in the further development of the chemistry of camphor and of the terpenes, it appears desirable to give in greater detail the methods used in their preparation.

The investigation of some of the derivatives of cyclopentanone involved has also led to the discovery that some of them decompose in a manner which is, so far as I am aware, quite new.

Phosphorus Tribromide.—Fifty grams of yellow phosphorus were dissolved in 100 grams of carbon disulphide in a flask, the lip of which had been cut off. The flask was connected with an upright condenser by means of a piece of rubber tubing slipped over both. A little more than the theoretical amount of bromine (about 125 cc.) was measured into a drop-funnel which was then hung in the top of the condenser. The bromine was then allowed to drop as rapidly as possible without the escape of carbon disulphide or bromine vapors. The carbon disulphide boils from the heat of the reaction and, condensing above, dilutes the bromine as it flows down. The whole of the bromine may usually be added in forty to fifty minutes. The completion of the change of the phosphorus to the tribromide, is indicated sharply by a change from yellow to a reddish color. The solution is then distilled from a Ladenburg bulb till a temperature of 165° is reached. The residue is sufficiently pure for use. A small additional amount may be obtained by distilling, in the same manner, the portion which passes over, and the yield is then almost quantitative.

Isoamyl Bromide, $\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CHCH_2CH_2Br.$

[1] An account of the results of this investigation was given at the Chicago meeting of the Society but some details completed since then are included in the present paper.

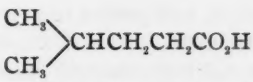
[2] *Am. Chem. J.*, **23**, 128; *Ber. d. chem. Ges.*, **33**, 54.

480 grams of fusel oil (boiling-point 128°–132° and consisting mainly of methyl-3-butanol,

were put in a flask and 437 grams of the phosphorus tribromide were added in portions, with constant cooling, the whole being added within half an hour. The mixture was allowed to stand over night and was then warmed for a couple of hours on the water-bath, a little water being added from time to time to prevent much evolution of hydrobromic acid. The evolution of hydrobromic acid indicates that the reaction takes place in part with the formation of esters of phosphorous acid, but the hydrobromic acid formed may, if retained, still react with the esters or with amyl alcohol. The mixture separated into two layers. The lower layer was separated and distilled slowly, with the addition of some pieces of porous tile to prevent bumping, till a temperature of 140° was reached by a thermometer in the liquid.

The distillate was mixed with the portion of isoamyl bromide previously separated, and the whole shaken twice with sulphuric acid which had been diluted with an equal volume of water, to remove hydrobromic acid, twice with concentrated sulphuric acid, to remove amyl alcohol, then with water and with a solution of sodium carbonate, and finally with dry sodium sulphate to dry and clear it. After filtering, it is sufficiently pure for the present use. Yield, 636 grams, or 88 per cent. of the theory.

Isocaproic Acid,

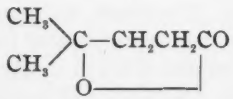


(methyl-4-pentanoic acid).—The only method of preparing isoamyl cyanide given by Beilstein, is from isoamyl chloride. The use of the bromide gives, in my experience, at least, very much better yields. For the preparation of isocaproic acid, the separation of the cyanide is not necessary. 280 grams of potassium cyanide were dissolved in 300 cc. of hot water, 1250 cc. of alcohol, and 636 grams of amyl bromide were added, and the whole boiled on a water-bath in a flask connected with an upright condenser for twenty-four hours. The solution was then poured from the potassium bromide, which separated, into a second flask

containing 350 grams of caustic potash, and the boiling continued for twenty-four hours longer. The solution was transferred to a large porcelain dish and evaporated with the addition of water, till the alcohol was removed. The residue was transferred to a flask containing 400 cc. of dilute sulphuric acid (1:1 by volume), and the isocaproic acid, which separated, was distilled. The acid solution was extracted once with ligroin. The yield was 401 grams, or 82 per cent. of the theory.

The method here given for the preparation of isocaproic acid may be used with advantage in the preparation of other acids and especially in the preparation of propionic acid, but requires some modification in details.

Isocaprolactone,



(4-methyl-1.4-pentanolide).—300 grams of isocaproic acid and 150 grams of sodium hydroxide were dissolved in 900 cc. of water, the solution was cooled, and 4.5 liters of a 10 per cent. slightly warm solution of potassium permanganate were added in portions of 500 cc. at a time, at intervals of one-half hour to one hour. Considerable heat is produced by the reaction and external heating is not necessary. A temperature of 50°–60° seems to be most desirable. The final decolorization of the permanganate may be hastened by warming on the water-bath. The filtrate and washings from the oxides of manganese were concentrated to about 600 cc. and poured into 350 cc. of dilute sulphuric acid (1:1 by volume). The mixture of isocaproic acid and lactone was separated from the acid solution and the latter was distilled with steam till about a liter had passed over. The mixture of acid and lactone was shaken with the distillate in portions of 300 cc. at a time, separating the aqueous solution each time, and then with water in the same manner till 4 or 5 liters have been used. By this treatment the lactone gradually passes into the aqueous solution, while most of the unchanged isocaproic acid remains behind. If an emulsion forms, a little ligroin can be added to clear the solution and does not seem to interfere with the extraction of the lactone by the water.

If desired, the amounts of acid and lactone in the successive

aqueous extracts can be followed approximately by titrating with tenth-normal caustic potash, with phenolphthalein as an indicator. The direct titration of the cold solution gives the amount of acid; then on adding an excess of the alkali, warming in a covered flask on the water-bath for a few minutes, and titrating back with tenth-normal acid, the difference between the excess of alkali added and the acid used, corresponds to the amount of lactone present.

The residual isocaproic acid is distilled to a temperature of 190° to remove the ligroin, and may then be used for a new oxidation.

The aqueous solution is then made strongly alkaline with sodium hydroxide, making sure enough is present to combine with all of the lactone, and warming the solution at first in a flask to avoid loss. It is then evaporated to a volume of 200 cc. or less, poured into dilute sulphuric acid, the mixture of acid and lactone separated, and the solution extracted several times with ether.

The mixture of lactone and acid is then exactly neutralized with a 30 per cent. solution of potassium hydroxide, added in portions, the mixture being shaken and cooled quickly after each addition. Fifteen to 20 grams of dry potassium carbonate are added and the solution is extracted repeatedly with ether. After extraction the alkaline solution is acidified, the isocaproic acid, which separates, is added to the mixture of lactone and acid obtained by a new oxidation, and the aqueous solution is also distilled with steam to recover some of the lactone which it retains.

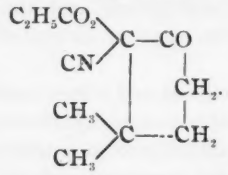
The ethereal solutions are dried with a little sodium sulphate and distilled. If enough potassium carbonate was used to remove all of the isocaproic acid a pure lactone is obtained by one distillation. The boiling-point is 208°–208°.5 and the melting-point 10°. Bredt and Fittig give the boiling-point as 207°[1] and melting-point as 7°–8°.[2] The yield is 35 to 40 per cent. of the portion of the isocaproic acid oxidized. Bredt and Fittig obtained a yield of 25 to 30 per cent.

γ-Chloroisocaproic Ester,[3]

1 *Ann. Chem* (Liebig), **208**, 56.
2 *Ibid.*, **200**, 260.
3 Bredt: *Ber. d. chem. Ges.*, **19**, 514.

In the original synthesis of trimethylcyclopentanone the γ-bromisocaproic ester was used. It has been found that better yields are obtained by the use of the corresponding chlorine derivative. Fifty grams of the lactone were mixed with 150 cc. of absolute alcohol and the solution in a bottle, surrounded with cold water, was saturated with hydrochloric acid gas, from 90 to 100 grams being required. After standing over night the solution was poured on crushed ice, the ester, which separated, washed two or three times with a little salt water, dried with sodium sulphate and filtered. The aqueous solution was extracted two or three times with low boiling ligroin, the ligroin being distilled away under diminished pressure. The yield is 71 to 73 grams, or 90 to 93 per cent. of the theory.

Dimethylcyancarboxethylcyclopentanone,



The preparation[1] of this substance and proof of its structure[2] have been given. In its further preparation, 250 grams of bromisocaproic ester gave 25 grams of the pure, crystallized substance. Better yields could probably be obtained by the use of the chlorisocaproic ester, but this has not been tried.

When the substance is boiled with dilute hydrochloric acid, it decomposes very slowly with evolution of carbon dioxide. In sealed tubes, at 150°–160°, the decomposition is more rapid, but still requires two or three hours. The products of decomposition are *acetic acid*, *isocaprolactone*, and *carbon dioxide*. The lactone boiled at 206°–209° and was analyzed, giving 62.83 per cent. of carbon and 8.62 per cent. of hydrogen. Theory requires 63.16 and 8.77 per cent. The silver salt gave 44.92 per cent. silver. Theory requires 45.19 per cent.

When saponified with alcoholic potash, *malonic acid*, melting at 133°, and *isocaprolactone*, boiling at 208°–209° and melting at 10°, were obtained.

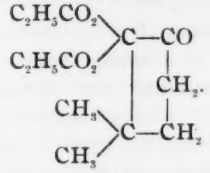
The decomposition here described is, of course, related to the

[1] *Am. Chem. J.*, **22**, 259.
[2] *Ibid.*, **23**, 135.

"acid decomposition" of acetacetic ester and its derivatives, but I do not recall any other case in which a carbon atom is removed from a ring and replaced by oxygen in this manner. A similar case will, however, be described further on, and the decomposition will, undoubtedly, be found typical for bodies of similar structure.

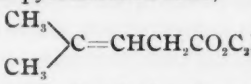
So far as the purpose of the experiments in working toward a synthesis of camphoric acid is concerned, the result was, of course, disappointing. At the end of a considerable amount of work, the original lactone was obtained instead of the dimethylcarboxethylcyclopentanone, which had been sought.

3,3-Dimethyl 2,2-dicarboxethyl cyclopentanone,



115 grams of sodium were dissolved in 130 cc. of absolute alcohol, 85 grams of *pure*[1] malonic ester were added and 89 grams of the γ-chloroisocaproic ester. The mixture was heated on the water-bath from four to six hours; most of the alcohol was then distilled by heating on the water-bath under diminished pressure. The residue was cooled, water added, and the oil which separated was dried with sodium sulphate and fractioned under diminished pressure, the lower boiling portions being distilled twice. The aqueous solution was also extracted once or twice with ether.

The portion boiling below 80° under a pressure of 20 mm., consists mainly of pyroterebinic ester,

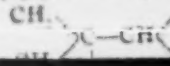


that from 90° to 100° of malonic ester with some chlorisocaproic ester, and that from 170°–180° of the dimethyldicarboxethylcyclopentanone. The yield of the last compound was about 20 per cent of the weight of the chlorisocaproic ester used.

[1] When malonic ester is prepared by the method described in this Journal, **18**, 1105 (1896), it contains considerable amounts of cyanacetic ester, and the conversion to malonic ester is not complete after many hours' heating of the acid-alcoholic solution. The ester prepared by Claissen's method, *Ann. Chem.* (Liebig), **218**, 131, would probably contain some of the same impurity. For the present purpose a pure ester prepared from calcium malonate is required.

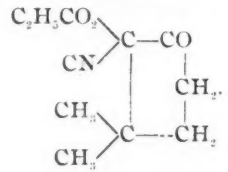
The pyroterebinic ester may be saponified with alcoholic potash, the pyroterebinic acid converted into isocaprolactone by boiling for a short time with dilute sulphuric acid (1 : 1 by volume) and the latter purified by treatment with potassium hydroxide and

Triethyl Ester of 3,3-Trimethylhexanoic, 1,2',6 Acid.



In the original synthesis of trimethylcyclopentanone the γ-bromisocaproic ester was used. It has been found that better yields are obtained by the use of the corresponding chlorine derivative. Fifty grams of the lactone were mixed with 150 cc. of absolute alcohol and the solution in a bottle, surrounded with cold water, was saturated with hydrochloric acid gas, from 90 to 100 grams being required. After standing over night the solution was poured on crushed ice, the ester, which separated, washed two or three times with a little salt water, dried with sodium sulphate and filtered. The aqueous solution was extracted two or three times with low boiling ligroin, the ligroin being distilled away under diminished pressure. The yield is 71 to 73 grams, or 90 to 93 per cent. of the theory.

Dimethylcyancarboxethylcyclopentanone,



The preparation[1] of this substance and proof of its structure[2] have been given. In its further preparation, 250 grams of bromisocaproic ester gave 25 grams of the pure, crystallized substance. Better yields could probably be obtained by the use of the chlorisocaproic ester, but this has not been tried.

When the substance is boiled with dilute hydrochloric acid, it decomposes very slowly with evolution of carbon dioxide. In sealed tubes, at 150°–160°, the decomposition is more rapid, but still requires two or three hours. The products of decomposition are *acetic acid*, *isocaprolactone*, and *carbon dioxide*. The lactone boiled at 206°–209° and was analyzed, giving 62.83 per cent. of carbon and 8.62 per cent. of hydrogen. Theory requires 63.16 and 8.77 per cent. The silver salt gave 44.92 per cent. silver. Theory requires 45.19 per cent.

When saponified with alcoholic potash, *malonic acid*, melting at 133°, and *isocaprolactone*, boiling at 208°–209° and melting at 10°, were obtained.

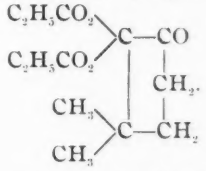
The decomposition here described is, of course, related to the

[1] *Am. Chem. J.*, **22**, 259.
[2] *Ibid.*, **23**, 135.

"acid decomposition" of acetacetic ester and its derivatives, but I do not recall any other case in which a carbon atom is removed from a ring and replaced by oxygen in this manner. A similar case will, however, be described further on, and the decomposition will, undoubtedly, be found typical for bodies of similar structure.

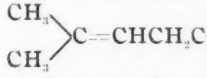
So far as the purpose of the experiments in working toward a synthesis of camphoric acid is concerned, the result was, of course, disappointing. At the end of a considerable amount of work, the original lactone was obtained instead of the dimethylcarboxethylcyclopentanone, which had been sought.

3,3-Dimethyl 2,2-dicarboxethyl cyclopentanone,



115 grams of sodium were dissolved in 130 cc. of absolute alcohol, 85 grams of *pure*[1] malonic ester were added and 89 grams of the γ-chloroisocaproic ester. The mixture was heated on the water-bath from four to six hours; most of the alcohol was then distilled by heating on the water-bath under diminished pressure. The residue was cooled, water added, and the oil which separated was dried with sodium sulphate and fractioned under diminished pressure, the lower boiling portions being distilled twice. The aqueous solution was also extracted once or twice with ether.

The portion boiling below 80° under a pressure of 20 mm., consists mainly of pyroterebinic ester,



that from 90° to 100° of malonic ester with some chlorisocaproic ester, and that from 170°–180° of the dimethyldicarboxethylcyclopentanone. The yield of the last compound was about 20 per cent of the weight of the chlorisocaproic ester used.

[1] When malonic ester is prepared by the method described in this Journal, **18**, 1105 (1896), it contains considerable amounts of cyanacetic ester, and the conversion to malonic ester is not complete after many hours' heating of the acid-alcoholic solution. The ester prepared by Claissen's method, *Ann. Chem.* (Liebig), **218**, 131, would probably contain some of the same impurity. For the present purpose a pure ester prepared from calcium malonate is required.

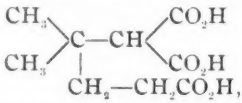
The pyroterebinic ester may be saponified with alcoholic potash, the pyroterebinic acid converted into isocaprolactone by boiling for a short time with dilute sulphuric acid (1 : 1 by volume) and the latter purified by treatment with potassium hydroxide and potassium carbonate as before. The recovered malonic ester may, of course, be used repeatedly.

Dimethyldicarboxethylcyclopentanone is a nearly colorless oil which boils at 167°–169° under a pressure of 14 mm.

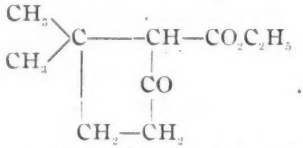
0.1831 gram gave 0.1328 gram water and 0.4086 gram carbon dioxide.
0.2208 gram gave 0.1594 gram water and 0.4892 gram carbon dioxide.

	Calculated for $C_{13}H_{20}O_5$.	Found. I.	II.
Carbon.....	60.94	60.83	60.43
Hydrogen	7.77	8.06	8.02

When dimethyldicarboxethylcyclopentanone is saponified by warming with an excess of alcoholic potash or soda, it breaks down in the same manner as dimethylcyancarboxethylcyclopentanone (p. 396), giving malonic and hydroxy isocaproic acids. In some cases, by careful saponification in a cold solution, there was obtained a small amount of the tribasic acid

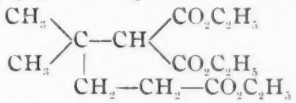


and at one time it was thought that this acid was formed by the saponification of the cyclic compound. A further study of the matter, however, makes it very probable that the tribasic acid was formed chiefly, if not altogether, from a small amount of the ester of that acid which had failed to condense to the cyclic compound. In one case, a considerable amount of dimethyladipic acid was found among the products of the saponification. This indicates that the cyclic compound had, in part, undergone the ketonic decomposition, giving the compound



This would then saponify to $\beta\beta$-dimethyladipic acid. It is also possible, however, that the ester of the tribasic acid decomposes partly on distillation, forming the ester of dimethyladipic acid.

Triethyl Ester of 3,3-Trimethylhexanoic, 1,2',6 Acid.



When 8.5 grams of sodium are dissolved in 140 cc. of absolute alcohol and the solution is dropped slowly, during two or three hours, into a mixture of 66 grams of chlorisocaproic ester and 75 grams of pure malonic ester, the ester of the tribasic acid is formed and its condensation to the cyclic ester is largely prevented. After heating for an hour longer, the product was treated as described above under the cyclic compound. Ten grams of the ester boiling at 150°–172°, under a pressure of 15 mm., were obtained. The boiling-point is apparently very nearly the same as that of the dimethyldicarboxethylcyclopentanone. Analysis I, below, was made with the ester prepared as described, and distilled but once. Analysis II was with an ester prepared from the pure crystallized acid by treatment with alcohol and hydrochloric acid as usual.

I. 0.2467 gram gave 0.1865 gram water and 0.5374 gram carbon dioxide.
II. 0.1612 gram gave 0.1276 gram water and 0.3521 gram carbon dioxide.

	Calculated for $C_{15}H_{26}O_6$.		Found.	
			I.	II.
C_{15} =	180 = 59.60		59.00	59.58
H_{26} =	26 = 8.61		8.40	8.80
O_6 =	96 = 31.79			
	302			

33-*Trimethylhexanoic*-1,2',6 *Acid*, obtained from the ester by saponification, crystallizes from water in compact crystals which melt at 165°–175° with decomposition, the temperature of melting being dependent on the rate of heating. The acid is very difficultly soluble in ether, and rather difficultly soluble in cold water.

0.2791 gram gave 0.1629 gram water and 0.5047 gram carbon dioxide.

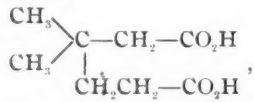
	Calculated for $C_9H_{14}O_6$.	Found.
Carbon	49.54	49.32
Hydrogen	6.42	6.49

The *calcium salt*, $Ca_3(C_9H_{11}O_6)_2 + 5H_2O$, was prepared by dissolving the acid in ammonia, adding calcium chloride and heating the solution on the water-bath. The salt which separated was filtered off, dissolved in cold water and the salt precipitated a second time by warming and evaporating the solution. The salt

is moderately soluble in cold water, and much less soluble in hot water. The portion which separates on warming the solution dissolves on cooling, while the calcium salt of dimethyladipic acid, which separates on warming, does not redissolve on cooling. These facts may be used to advantage in separating mixtures of the two acids.

The salt dried over sulphuric acid lost 13.69 per cent. water. Theory requires for $5H_2O$ 14.06 per cent. The dry salt gave 21.79 per cent. calcium. Theory requires 21.81 per cent.

ββ-Dimethyladipic Acid,



is formed quantitatively, when the acid last mentioned is heated for a short time to 200°. The acid is easily soluble in hot water and in ether, difficultly soluble in cold water, and almost insoluble in ligroin. It crystallizes from water in small plates. It melts at 102°.

0.2052 gram gave 0.1490 gram water and 0.2160 gram carbon dioxide.
0.1934 gram gave 0.1401 gram water and 0.3926 gram carbon dioxide.

	Calculated for $C_8H_{14}O_4$.	Found. I.	II.
Carbon.....	55.17	55.29	55.36
Hydrogen.....	8.05	8.07	8.05

0.1136 gram of the acid took 13.13 cc. tenth-normal caustic potash. Theory requires 13.05 cc.

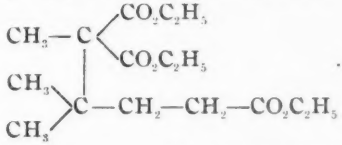
The *calcium salt*, $Ca(C_8H_{12}O_4)+nH_2O$, is most easily prepared by dissolving the acid in ammonia, adding calcium chloride and boiling the solution. No precipitate forms till the solution is warmed. The salt, when once formed, is difficultly soluble but may be crystallized by evaporating its solution, when it is deposited in pearly scales. The salt prepared in this manner lost 21.99 per cent. of water at 140°, while that prepared by precipitation lost only 6.18 per cent. The dried salts gave, respectively, 18.72 and 19.16 per cent. of calcium. Theory requires 18.87 per cent.

The *silver salt* was prepared by adding silver nitrate to a solution of the calcium salt. It is almost entirely insoluble in water. The analysis gave 55.38 per cent. silver. Theory requires 55.67 per cent.

The *copper salt* is precipitated as a green powder on adding copper acetate to an aqueous solution of the acid.

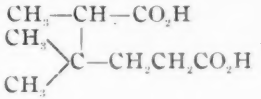
Some time ago Tiemann[1] obtained from ionone an acid which he supposed to be $\beta\beta$-dimethyladipic acid and which melted at 87°. The $\alpha\alpha$-dimethyladipic acid which he describes melts at the same temperature.[2] Baeyer[3] has also obtained a dimethyladipic acid which melts at 87°–88° by the oxidation of tetrahydroeucarvone. He seems to imply that his acid is the $\beta\beta$-acid but does not make a definite statement to that effect. Since $\beta\beta$-dimethyladipic acid contains no asymmetric carbon atom, stereoisomerism is extremely improbable and no evidence of its existence has appeared in my study of the body. It would seem, therefore, that if the acids obtained by Tiemann and Baeyer were pure, they must possess another structure than that ascribed to them.

Triethyl Ester of 2,33-*Trimethylhexanoic* 1,2',6 *Acid*,



The preparation of this compound by the condensation of γ-bromisocaproic ester with the diethyl ester of methyl malonic acid has been described.[4] It has been found that to obtain a pure product, the methyl malonic acid must be purified by crystallization from water[5] and so freed from malonic acid, which it will contain if prepared by the condensation of malonic ester with methyl iodide. The yield is improved somewhat by the use of γ-chlorisocaproic ester in place of the bromine derivative but it is always poor. A better method of preparation consists in the condensation of the triethyl ester of the trimethyl hexanoic acid described above (p. 399) with methyl iodide by means of sodium ethylate.

$\alpha\beta\beta$-Trimethyladipic Acid,



[1] *Ber. d. chem. Ges.*, **31**, 860, 884.
[2] *Ibid.*, **31**, 883.
[3] *Ibid.*, **31**, 2074.
[4] *Am. Chem. J.*, **23**, 128.
[5] Perkin: *J. Chem. Soc.* (London), **45**, 570.

This acid is formed when the 33-trimethylhexanoic-1,2',6 acid is heated for a short time to 200°. It appears to exist in two forms, a fumaroid and a maleïnoid form. Only the former has thus far been obtained pure. The acid was purified by crystallization from water and from ether. It is difficultly soluble in cold water and in ether, almost insoluble in ligroin. It crystallizes from water or from ether in leaflets which melt at 136°.

0.1637 gram of the acid gave 0.1286 gram water and 0.3424 gram carbon dioxide.

	Calculated for $C_9H_{16}O_4$.	Found.
Carbon	57.44	57.04
Hydrogen	8.52	8.73

ROSE POLYTECHNIC INSTITUTE, TERRE HAUTE, IND., April 25, 1901.

[CONTRIBUTION FROM THE CHEMICAL DIVISION, U. S. DEPARTMENT OF AGRICULTURE, NO. 41.—SENT BY H. W. WILEY.]

A NEW INDICATOR FOR USE IN DETERMINING TOTAL ACIDITY OF WINES.[1]

BY E. G. RUNYAN.

Received May 11, 1901.

IN maintaining a chemical control of a beet sugar house, it is often necessary to determine by some rapid method the excess of alkali in the juices, sirups, and massecuites. The usual method is to titrate the material with a standard acid solution. As these products vary in color from a light amber to a dark brown, or nearly black, the ordinary indicators often give very unsatisfactory results, or fail entirely, on account of the difficulty of noting the end reaction.

To meet this difficulty, a French chemist, L. Lachaux, in 1892, proposed a mixture of corallin and malachite green[2] prepared as follows:

Three and one-tenth grams of corallin or commercial rosolic acid are dissolved in 150 cc. of 90 per cent. alcohol, neutralized and mixed with 0.5 gram malachite green dissolved in 50 cc. of alcohol. With this mixture, alkalies give a purple color, which is changed to a green by acids.

Malachite green dissolves in alcohol yielding a greenish blue

[1] Read before the Washington Section of the American Chemical Society, March 14, 1901.

[2] The zinc-double-chloride of tetramethyldi-*p*-amidotriphenyl-carbinol, $(C_{23}H_{23}N_2Cl_4)_2 + 2ZnCl_2 + 2H_2O$.

solution, which possesses no value as an indicator by itself, but when mixed with corallin it blends with the colors of that indicator and renders the end reaction more distinct. As only the corallin in this mixture acts as an indicator, it follows that this corallin-malachite mixture can be used in titrating only those acids and bases which give a distinct end reaction with corallin alone.

Recently I had occasion to make use of this indicator in determining the amount of alkali in a highly colored sample of beet molasses and obtained very satisfactory results. It occurred to me at once that this indicator might be used advantageously in determining the total acidity of such highly colored products as wines, vinegars and ciders, since, as is well known, the present methods are far from satisfactory in the case of red or highly colored wines. The method adopted by the Association of Official Agricultural Chemists for the determination of total acidity in wines is as follows:

"Transfer 10 cc. of the sample to a beaker, and in case of white wines add about 10 drops of a neutral litmus solution, and titrate with decinormal sodium hydroxide solution until the red color changes to violet. In case of red wines, continue adding a few drops at a time of alkali solution, until a drop of the mixture placed on delicate red litmus paper shows an alkaline reaction."

Another method in use by some chemists is to dilute 10 cc. of the wine to about 300 cc. with boiling distilled water, heat the mixture to boiling for a moment to expel carbon dioxide, add a few drops of phenolphthalein solution and titrate with decinormal sodium hydroxide solution.

Any one who has ever tried either one of the above methods with a claret or other red wine, will, I think, agree with me that the determination of the exact point of neutrality is very uncertain.

To test the corallin-malachite indicator in comparison with phenolphthalein and litmus, three samples of wine were procured: (1) a claret, as a type of red wine; (2) a Rhine wine for the white type; and (3) a sherry for the medium color. In this experiment the following method was employed:

Transfer 10 cc. of the sample to a beaker, dilute with about 300 cc. of boiling distilled water, heat the mixture to boiling for a moment to expel all carbon dioxide, cool to about 75°, add 10 drops of the corallin-malachite solution, then add an excess of

decinormal sodium hydroxide solution, indicated by a purple color, titrate the excess of alkali with decinormal acid solution, adding the acid solution slowly until the appearance of a distinct green color. The change in color is best observed by transmitted light. A trial showed that it was easier to detect the transition from the alkali to the acid side than the reverse.

With phenolphthalein and litmus, slightly more of the indicator was used and the decinormal soda solution added slowly to the point of neutrality as near as that could be determined. The results are expressed as usual in terms of tartaric acid, 1 cc. decinormal sodium hydroxide solution = 0.0075 gram tartaric acid. The following are the results obtained:

GRAMS TARTARIC ACID IN 100 CC. OF WINE.

Wine.	Corallin Malachite.	Phenolphthalein.	Litmus.
1. Claret	0.840	0.995	0.890
	0.870	0.980	0.920
	0.870	0.980	....
	0.880	....	....
	0.875	....	....
Average	0.867	0.985	0.905
2. Rhine wine	0.705	0.730	0.730
	0.710	0.725	0.720
	0.705	0.730	0.725
	0.695	0.735	....
	0.705	....	....
	0.705	....	....
	0.695	....	....
Average	0.703	0.730	0.725
3. Sherry	0.450	0.490	0.475
	0.430	0.475	0.460
	0.440	0.475	0.460
	0.445	0.475	0.460
	0.435	....	....
	0.430	....	....
Average	0.438	0.479	0.464

The results obtained with corallin-malachite are invariably lower than those obtained with the other indicators, but this was to be expected when we consider that with the corallin-malachite the titration was made toward the acid reaction, and with the other indicators it was made toward the alkali side.

The greatest difference appears in the results on the claret or

red wine, where in case of phenolphthalein and litmus it was necessary to add a decided excess of alkali before the change of color could be detected. I am inclined, therefore, to believe that the results with corallin-malachite more nearly represent the true figure for total acidity of this sample.

To test the sensitiveness of the corallin-malachite, 5 drops of the mixture were added to 100 cc. of distilled water, when 0.1 cc. of 0.01 normal hydrochloric acid solution or 0.01 normal sodium hydroxide solution was sufficient to give a distinct acid or alkali reaction.

In the presence of other coloring-matters, slightly more of the standard solutions was required.

In consideration of the encouraging results obtained with this corallin-malachite mixture in my hands, I feel justified in recommending this indicator to the attention of chemists engaged in the analysis of wines, vinegars, ciders, and similar products.

THE ESTIMATION OF CARBONIC ACID IN WATER.

By Joseph W. Ellms and Jay C. Beneker.

Received May 10, 1901.

THE estimation of carbonic acid is of considerable importance in the technical analysis of water. In the softening of water for manufacturing purposes and in the purification of public water supplies, where certain processes are employed, an accurate knowledge of the amount of this constituent is essential to a proper treatment of the water. Moreover in the sanitary analysis of sewage, of effluents from sewage purification plants, and of polluted waters generally, a determination of the amount of carbonic acid present may throw considerable light on the nature and extent of the chemical and bacterial changes which are taking place.

CONDITION IN WHICH CARBONIC ACID EXISTS IN NATURAL WATERS.

Before discussing the methods usually employed for the estimation of carbon dioxide in water, and the principles upon which these methods are based, it may be well to consider in what forms of combination carbon dioxide exists in water and to define the different terms which are used to designate them.

The carbonates which are commonly found in natural waters are those of calcium and magnesium. The normal carbonates of

these bases are, relatively speaking, but sparingly soluble in water. If, however, more than enough carbon dioxide be present to unite with the oxides of calcium and magnesium to form the compounds $CaCO_3$ and $MgCO_3$, the solubility of these salts is much increased. It is generally assumed, that when there is present one extra molecule of carbon dioxide for each molecule of calcium carbonate or of magnesium carbonate, compounds of the character of sodium bicarbonate exist, although such salts have never been isolated. These salts are presumed to have the composition represented by the formulas $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$, respectively.

The gas carbon dioxide (CO_2) is quite soluble in water and therefore may exist in natural waters in amounts greater than is required to form the bicarbonates of the alkaline earth bases which may be present. It is usually considered that carbon dioxide thus dissolved in the water exists as a true acid having the formula H_2CO_3.

From the above it is evident that there are three conditions in which carbon dioxide may be present in natural waters. If the carbon dioxide is not combined with any base, it is spoken of as "free carbonic acid;" if it is combined indirectly with the base as in the form of the bicarbonates, it is termed "half bound carbonic acid;" and if directly united to the bases as in calcium and magnesium carbonates, it is called "fixed carbonic acid." The sum of the amounts of the carbonic acid found in these three forms is usually spoken of as the "total carbonic acid." The carbonic acid that is expelled on heating aqueous solutions containing either "free" or "half-bound carbonic acid" or both is sometimes spoken of as "volatile carbonic acid."

Natural waters carry varying amounts of carbonic acid, depending on the character of the geological formations with which they have come in contact. Ground waters having probably been under greater pressure usually contain more carbonic acid than surface waters. Moreover ground waters which become exposed to the air lose the larger proportion of their free carbonic acid and may even part with some of their half-bound and fixed carbonic acid. The loss of the latter results, of course, from a precipitation of carbonates (calcium carbonate principally), as a result of the loss of some of the half-bound carbonic acid.

It was found that the ordinary distilled water of the laboratory

might contain from 6 to 10 parts per million of free carbonic acid. It was necessary to boil off 10 to 15 per cent. of the original volume of such a water in order to free it completely from the gas. A water thus freed from carbonic acid absorbs, when exposed to the air, more or less carbon dioxide depending on the amount present and on the temperature and pressure. Two samples of distilled water free from carbonic acid were exposed in beakers to the air of the laboratory in which the temperature was approximately 16° C.

	A. Free carbonic acid. Parts per million.	B. Free carbonic acid. Parts per million.
Original water	0	0
After twenty-four hours	2.2	2.2
After forty-eight hours	15.0	13.2
After seventy-two hours	0.9	0.9

The great variation in the amounts obtained was probably due to the differing quantities of carbonic acid present in the atmosphere of the laboratory on the particular day the samples were examined. On the second day a carbonic acid generator was being used in the laboratory and considerable gas was also being burned.

Waters containing large amounts of calcium bicarbonate and free carbonic acid, not only lose their free but also a portion of their half-bound carbonic acid, when exposed to the air for any length of time. The excess of calcium carbonate ($CaCO_3$) is thereby precipitated and the solution grows weaker in lime, until a state of equilibrium is reached.

The following experiments illustrate the action of a strong solution of calcium bicarbonate ($Ca(HCO_3)_2$), when exposed to the air of the laboratory.

	A. Carbonic acid in solution. Parts per million.			B. Carbonic acid in solution. Parts per million.		
	Free.	Half-bound.	Fixed.	Free.	Half-bound.	Fixed.
Original water	52.8	109.4	109.4	52.8	109.4	109.4
After twenty-four hours	7.9	....	....	7.0	....	....
After forty-eight hours	1.3	....	....	1.1	....	....
After seventy-two hours	0	80.7	84.5	0	80.7	84.5

Magnesium bicarbonate is much more soluble in water than calcium bicarbonate, but strong solutions show the same tendency to give up their half-bound carbonic acid as do strong solutions of calcium bicarbonate. This occurs, however, without any precipitation of magnesium carbonate ($MgCO_3$) because the latter itself is quite soluble in water.

A strong solution of magnesium bicarbonate lost all of its free and 12 per cent. of its half-bound carbonic acid in less than three days when exposed to the air of the laboratory. This solution, therefore, contained 12 per cent. of its total magnesium carbonate in the form of normal magnesium carbonate ($MgCO_3$). On the other hand the calcium bicarbonate solution, as shown above, contains only 4 per cent. of its total calcium carbonate in the form of the normal carbonate ($CaCO_3$). This illustrates the difference in degree of the affinity of solutions of these two salts for carbon dioxide.

However solutions of calcium and magnesium carbonate which contain no half-bound or free carbonic acid or only very limited amounts of the former, tend to absorb the gas from the air, and thus form the bicarbonates of these bases. Calcium carbonate solutions in time become acid (*i. e.*, contain free carbonic acid), but the acidity is always very slight and the state of equilibrium seems to be reached when the lime is all in the form of the bicarbonate. On the contrary weak solutions of magnesium carbonate, while they absorb carbon dioxide from the air to form magnesium bicarbonate, only very slowly approach the condition where all the magnesium exists as bicarbonate; in fact the tendency seems to be for the solution to remain as a mixture of these two compounds. That these facts have a bearing on certain classes of natural waters will be shown later.

PRINCIPLES ON WHICH METHODS FOR THE ESTIMATION OF CARBONIC ACID ARE BASED WITH A DISCUSSION OF THE ERRORS AFFECTING THEIR ACCURACY.

A comparison of the three most commonly employed volumetric methods for the determination of carbonic acid in water, has been made by the writers, with the purpose of discovering, if possible, the sources of error which affected each of them, and also to learn which gave results closest to amounts actually known to be present in solution.

The oldest and best known of the three methods was suggested by Pettenkofer.[1] Trillich[2] modified this method in order to avoid certain difficulties arising in the original method, and as this modification is quite radical, the process as carried out by him

[1] *N. Rep. Pharm.*, **10**, 1.

[2] *Ztschr. angew. Chem.*, June 15, 1889, p. 337.

can be considered practically as a new method. Seyler[1] advocates what he terms the Lunge-Trillich method, which in principle differs materially from that of Pettenkofer's or Trillich's modification of Pettenkofer's method.

These three methods were those which were investigated and compared. In order to avoid confusion the three will be designated in this paper as Pettenkofer's, Trillich's, and Seyler's methods respectively.

PETTENKOFER'S AND TRILLICH'S METHODS.

The estimation of the carbonic acid in natural waters consists in determining the amount of half-bound and free carbonic acid which may be present. The estimation of the fixed carbonic acid is generally regarded as a separate determination, and is not commonly included in the statement of the results.

The principle upon which Pettenkofer based his determination depends on the action which the barium or calcium hydroxide has upon free and half-bound carbonic acid, whereby insoluble calcium and barium carbonates are formed which precipitate out of solution. Either calcium or barium hydroxide may be used, the reactions involved being of similar character.

As an excess of the precipitant is used, the portion unacted upon is determined volumetrically with a standard acid solution, and the amount of the barium or calcium hydroxide which has reacted with the free and half-bound carbonic acid can thus be determined by difference. The reaction is as follows:

$$Ca(HCO_3)_2 + CO_2 + 2BaO_2H_2 = 2BaCO_3 + CaCO_3 + 2H_2O.$$

As the calcium carbonate present has been held in solution by the assistance of the half-bound molecule of carbon dioxide, it also precipitates upon the latter's removal by the barium hydroxide.

In so far as that portion of the half-bound carbonic acid, which may be present in a natural water, is combined with the magnesium carbonate to form the bicarbonate, the reaction between it and the calcium or barium hydroxide is the same as shown by the above reaction. But magnesium carbonate ($MgCO_3$) instead of precipitating out as such, reacts with the calcium or barium hydroxide and forms magnesium hydroxide, which latter, being insoluble, precipitates. The presence, therefore, of magnesium carbonate or in fact any magnesium salt causes the calcium or

[1] *Chem. News*, **70**, 104 (1894); and *Analyst*, **22**, 312 (1897).

barium hydroxide to be used up. Pettenkofer avoids the precipitation of the magnesium by the introduction of ammonium chloride, which, by forming a soluble salt of ammonium and magnesium chloride, prevents any loss of calcium or barium hydroxide. The reaction is as follows:

$$MgCO_3 + 4NH_4Cl + BaO_2H_2 = MgCl_2(NH_4Cl)_2 + BaCO_3 + 2NH_4OH.$$

An equivalent amount of ammonium hydroxide being formed, no change in the caustic alkalinity of the sample results.

Trillich's modification of Pettenkofer's method consists in not attempting to prevent the reaction between the magnesium salts and the caustic alkali by the addition of ammonium chloride, but in allowing the precipitation to take place. From a direct gravimetric determination of the amount of the magnesium present in another portion of the sample, he is enabled to apply the proper correction to the result obtained volumetrically. Since 40 parts of magnesium oxide (MgO) would react with as much barium or calcium hydroxide as 44 parts of carbon dioxide, the correction is obtained by multiplying each part of magnesium oxide (MgO) present by 1.1 and subtracting the product from the apparent amount of carbonic acid found by the volumetric determination. Trillich's method, therefore, only differs from the original Pettenkofer method in providing another way to overcome the difficulty arising from the presence of magnesium salts.

In order to differentiate between the free, half-bound, and fixed carbonic acid, Trillich uses that portion of his solution which contains the precipitated carbonates and titrates it with hydrochloric acid and cochineal. From this he obtains the "total carbonic acid." By subtracting the "free and half-bound carbonic acid" from this, he obtains the "fixed carbonic acid;" and by finding the difference between the "free and half-bound acid" and the "fixed" (equivalent to the half-bound), he estimates the "free carbonic acid."

It is apparent that by this means the various forms of carbonic acid may be determined in Pettenkofer's method, although the writers are not aware that originally any such differentiation was attempted. Moreover it would seem more simple to use a method which would not involve the objectionable titration of the suspended carbonates and magnesium hydroxide. This can be done by determining the fixed carbonic acid by direct titration of a

separate sample of the water by Hehner's method, and from this all the data given can easily be deduced. In our examination of these methods we have not attempted to carry out Trillich's titration of the portion of the sample containing the precipitated carbonates.

In Pettenkofer's method and in Trillich's as well, oxalic acid is used to titrate the excess of the barium or calcium hydroxide added to the water under examination. If barium hydroxide is used Trillich recommends that to each 9 grams of the barium hydroxide, 0.5 gram of barium chloride be added in order to convert the hydroxides of sodium and potassium, which are common impurities of barium hydroxide, into chlorides. The reason for this and for the addition of barium or calcium chloride in the original Pettenkofer method, is more fully stated by Fresenius[1] as follows:

"If ..... a water contains an alkali carbonate or any other alkali salt whose acid would be precipitated by lime or baryta, a neutral solution of calcium or barium chloride must be added to decompose the same. This addition, too, prevents any inconvenience arising from the presence of free alkali in the lime or baryta water, or of magnesium carbonate in the carbonic acid water; this inconvenience consists in the fact that oxalate of an alkali or of magnesium enters into double decomposition with calcium carbonate (which is seldom entirely absent from the fluid to be analyzed), forming calcium oxalate and carbonate of the alkali or of magnesium, which latter will of course again take up oxalic acid."

The details of the Pettenkofer process consist in taking 100 cc. of the water to be analyzed, placing it in a bottle, adding 3 cc. of barium chloride, 2 cc. of a saturated solution of ammonium chloride and 45 cc. of barium hydroxide solution. After allowing the mixture to stand about twelve hours closely stoppered, an aliquot portion of the clear supernatant liquid is pipetted off and titrated with oxalic acid. In our experiments an approximately 0.02 normal solution of sulphuric acid was used. The barium hydroxide solution was approximately 0.05 normal and the indicator employed was rosolic acid.

The Trillich method differs from the above in using 5 cc. of barium chloride in place of 3 cc., omitting the ammonium chloride and using phenolphthalein as the indicator. In titrating the

[1] "Quantitative Chemical Analysis," p. 405 (English edition, 1889).

suspended carbonates for the determination of the total carbonic acid, Trillich employs hydrochloric acid and cochineal as the indicator, as previously stated.

In carrying out these methods the following precautions have been found necessary in order to obtain uniform and consistent results.

1. The barium hydroxide solution (9 grams $BaO_2H_2.8H_2O$ and 0.5 gram $BaCl_2.2H_2O$ per liter) should be carefully filtered and kept in a bottle whose outlet to the air is provided with a U-tube containing fused calcium chloride and stick potash. A siphon tube conveniently conveys the liquid to the measuring burette. Solutions thus protected will keep for a long time without serious deterioration. A solution thus guarded from the atmospheric carbon dioxide was found at the end of fifty days to be 0.6 per cent. weaker than when first tested.

2. If oxalic acid is used, it should be frequently tested as it deteriorates rapidly. A solution containing 2.8636 grams per liter (1 cc. = 1 mg. CO_2) was found at the end of forty-five days to be 6.7 per cent. weaker and one fifty days old was 8.7 per cent. weaker.

3. Dry or well drained, ground glass-stoppered bottles with their stoppers well vaselined should be used for holding the samples. On account of the strong tendency which barium hydroxide solutions exposed to the air, show in the absorption of atmospheric carbon dioxide, the most erratic results will be obtained if the bottle stoppers are not tight-fitting.

4. Samples of water to be analyzed should properly, if at all high in free and half-bound carbonic acid, be introduced into the bottle by means of a siphon or tube, similar to the methods used in taking samples for determining dissolved oxygen.

5. After the introduction of the sample into the bottle, the other reagents should be added, the barium hydroxide solution, however, always being the last to be introduced. The barium hydroxide should be introduced by means of a long delivery tip on the burette, the lower end of which dips below the surface of the sample in the bottle. The barium hydroxide should be run in as quickly as possible and the bottle immediately stoppered and shaken.

6. The bottle should then be set aside to stand at least twelve hours and under no condition should the stopper be removed until

the clear supernatant liquid is pipetted off for immediate titration.

7. The removal of the 25 or 50 cc. of the liquid to be titrated should take place without stirring up the precipitate in the bottom of the bottle. This is extremely important and its neglect, even when only a slight amount of sediment is withdrawn, will lead to irregular and unreliable results.

8. The receptacle in which the titration takes place should be a narrow mouthed fairly long-necked flask, preferably of about 250 cc. capacity. The titration should take place immediately upon the withdrawal of the portion from the bottle and the acid should be run in quickly.

9. If the delivery of the acid can be quickly effected the larger portion should be delivered into the flask holding the barium hydroxide as soon as possible without any unnecessary shaking of the flask. The titration can then be cautiously completed. If, however, the burette delivers the acid slowly it is better to run into the empty flask the larger portion of the acid and then add the portion of the sample to be titrated. This avoids undue exposure of the caustic alkali to the air and consequently any carbonating of the barium hydroxide.

10. The standardization of the barium hydroxide solution by the acid should be carried out in a manner similar to the method employed in the titration of the sample. In standardizing the barium hydroxide solution in order to obtain its value in terms of the acid, it is necessary in the Pettenkofer method, that the titration should take place in the presence of ammonium chloride, if rosolic acid or any indicator which is at all affected by this salt, is used. Otherwise the value of the alkali in terms of the acid will be erroneous and the differences, though slight, will lead to considerable error.

In spite of the above precautions an error due to manipulation may arise on account of the extreme sensitiveness of barium hydroxide to atmospheric carbon dioxide. An average of twenty experiments made with the utmost caution, with boiled distilled water and barium hydroxide in well-ground glass-stoppered bottles, thoroughly vaselined, showed a loss of barium hydroxide equivalent to 1.5 parts per million of carbonic acid, with a range of from 1 to 3 parts per million.

Reinitzer[1] found in a solution of lime-water containing 1173.8

[1] *Zischr. angew. Chem.*, September 15, 1894.

parts per million of calcium oxide, carbon dioxide equivalent to (*a*) 8.7 parts and (*b*) 9.3 parts, respectively. The results were obtained by acidulation of the solution, expulsion of the carbon dioxide by heating, absorption and weighing of the gas in caustic potash. He states "we may assume the same conditions hold good with baryta water."

The writers have found carbonic acid in calcium hydroxide solutions to range from 0 to 6 or 7 parts per million, although on an average the quantity was less than 3 parts per million. In the case of barium hydroxide solutions we have never found over 1 part per million of carbonic acid and the average appears to be less than 0.5 part per million. The error arising, therefore, from dissolved carbonates in barium hydroxide solutions, in the absence of other salts which may effect their solution, we are inclined to believe may be usually disregarded as a source of error.

The presence of suspended carbonates in the portion of the sample being titrated, however, is a source of error which must be carefully avoided. This arises from the direct solution of these salts in the titrating acid; and this is true whether oxalic acid is used or sulphuric acid, which latter was employed by the writers. This is shown by the following experiments.

TABLE SHOWING SOLUBILITY OF SUSPENDED CARBONATES BY TITRATING ACID.

I. Acid Added to Alkali.

Sol. used. cc.	Containing no suspended carbonates. N 50 sulphuric acid. cc.	Containing suspended carbonates. N 50 sulphuric acid. cc.	Remarks.
10	3.9	5.0–	End-point indefinite with suspended carbonates.

Sol. used. cc.	N 20 (approx.) oxalic acid. cc.	N 20 (approx.) oxalic acid. cc.	
10	2.2	2.7+	End-point indefinite with suspended carbonates.

On another sample the following results were obtained:

I. Acid Added to Alkali.

Sol. used. cc.	Containing no suspended carbonates. N 50 sulphuric acid. cc.	Containing suspended carbonates. N 50 sulphuric acid. cc.	Remarks.
10	5.0	7.0+	End-point indefinite with suspended carbonates.

II. Alkali Added to Acid.

10	5.0	7.0+	End-point indefinite with suspended carbonates.

It will thus be seen that the presence of suspended carbonates is quite inadmissible if accurate results are to be expected.

In both Pettenkofer's and Trillich's methods, the chief disturbing element is magnesium. Its salts must either be kept in solution as in Pettenkofer's method by the use of ammonium chloride, or allowed to precipitate out and be corrected for as in Trillich's method. As the errors arising from the presence of magnesium salts are probably due to two different causes in the two methods, they will be discussed separately.

The erratic results often obtained with Pettenkofer's method are generally acknowledged. Tiemann[1] admits that duplicate results may vary from 5 to 10 parts per millon, and that the results are still more uncertain in the presence of magnesium salts. Thinking that ammonium chloride might be instrumental in holding carbonates in solution, some experiments were made to learn what effect it did have. The following experiments show the results obtained with a water which contained 59.2 parts per million of free and half-bound carbonic acid, but which contained no magnesium salts.

TABLE SHOWING EFFECT OF AMMONIUM CHLORIDE IN HOLDING CARBONATES IN SOLUTION.

No.	Sol. (approx. N/20) barium hydroxide. cc.	Saturated solution ammonium chloride. cc.	Carbonic acid (CO_2) obtained. Parts per million.
1	10	0	57.4
2	45	0	60.0
3	10	2	0.0[2]
4	20	2	0.0[3]
5	30	2	46.0
6	45	2	56.6

It will be noticed that as the concentration of the barium hydroxide solution increases, the ammonium chloride is less able to hold the carbonates in solution. Even with 45 cc. of barium hydroxide solution, the amount is still less than with the same amount of alkali where no ammonium chloride is present. It is apparent from these experiments that carbonates may be held in solution where the concentration of the barium hydroxide solution is not great enough; and such a condition might easily arise in a water containing low amounts of magnesium but considerable

[1] "Chem. Analyses des Wassers," Tiemann.

[2] In the third experiment no loss of barium hydroxide resulted and 38.4 parts per million of fixed carbonic acid were indicated in addition.

[3] No loss of barium resulted in the fourth experiment and 1.9 parts per million of fixed carbonic acid were found in addition.

carbonic acid, which latter would use up a large proportion of the barium hydroxide added.

In order to see whether ammonium chloride was able to hold in solution all of the magnesium which might be present, the following experiments were made:

TABLE SHOWING EFFECTIVENESS OF AMMONIUM CHLORIDE IN HOLDING MAGNESIUM SALTS IN SOLUTION.

Solution of magnesium sulphate. Total volume of solution equal to 150 cc.

Barium hydroxide sol. (approx. N 20). cc.	Saturated solution ammonium chloride. cc.	Magnesium oxide added. Parts per million.	Magnesium oxide precipitated. Parts per million.
45	0.5	27	2.0
45	0.5	27	1.4
45	0.5	91	9.4
45	2.0	27	0
45	2.0	27	0
45	2.0	91	0
	Solution of magnesium carbonate.[1]		
45	2.0	15	0
45	2.0	15	0
45	2.0	15	0

It is evident that 0.5 cc. of a saturated solution of ammonium chloride is not sufficient to hold in solution all the magnesium oxide that was added. Two cc. are, however, able to hold in solution at least 90 parts per million of the oxide without any of it precipitating.

In Trillich's method the magnesium salts are allowed to precipitate as magnesium hydroxide, and are then corrected for as previously stated. It is quite evident, therefore, that unless the precipitation is complete an error is introduced into the correction. The following experiments show that this precipitation is not complete under certain conditions.

TABLE SHOWING INCOMPLETE PRECIPITATION OF MAGNESIUM HYDROXIDE BY BARIUM HYDROXIDE.

Solution of magnesium carbonate containing 15 parts per million of magnesium oxide. Total volume of solution equal to 100 cc.

Barium hydroxide solution. cc.	Magnesium oxide precipitated. Parts per million.	Magnesium oxide not precipitated. Parts per million.
45	13.7	1.3
45	13.7	1.3
45	12.0	3.0
45	13.7	1.3
45	12.0	3.0
45	12.0	3.0
45	12.0	3.0
Average,	12.6	2.4

[1] Total volume of magnesium carbonate solution is equal to 100 cc.

From the above it will be seen that on an average 2.4 parts per million of magnesium oxide, equivalent to 2.6 parts per million of carbonic acid, were not precipitated in a solution containing 45 cc. of an approximately 0.05 normal solution of barium hydroxide in a total volume of 100 cc. From a large number of experiments made with a standard magnesium sulphate solution, it has been found that the same is true of this salt, *i. e.*, that the magnesium is but partially precipitated under certain conditions.

A large excess of barium hydroxide is necessary in order to effect practically complete precipitation, and unless this excess is maintained as the quantity of magnesium increases the quantity of magnesium which remains unacted upon will also increase.

This is well shown by the following table where constantly increasing amounts of magnesium were introduced into the solution.

TABLE SHOWING INCOMPLETE PRECIPITATION OF MAGNESIUM HYDROXIDE WITH CONTINUALLY INCREASING AMOUNTS OF MAGNESIUM SULPHATE.

Solution of magnesium sulphate. Total volume of solution equal to 100 cc.

Barium hydroxide solution. cc.	Magnesium oxide added. Parts per million.	Magnesium oxide precipitated. Parts per million.	Magnesium oxide not precipitated. Parts per million.
45	9.0	10	0
45	27.0	24	3.0
45	54.0	50	4.0
45	91.0	76	15.0

It will be noted that in the first sample, slightly more than the amount of magnesium oxide actually present appears to be precipitated. This seems to be characteristic of results obtained on samples in which the magnesium is in small amount while the barium hydroxide is in large excess. It is due to the fact that the loss of barium hydroxide by carbonating is always greater in such cases. The error from this cause, which may be called the "error of manipulation" and the error due to non-precipitation of magnesium hydroxide, act in opposite directions, the former tending to increase the apparent precipitation and the latter to decrease it. It is probable, therefore, that the quantity of magnesium oxide not precipitated may be greater than is indicated above.

How seriously this error may affect results is shown by the following table. A standard solution was prepared and was found to contain by Trillich's method, when no magnesium salts were present, 46.2 parts per million of free and half-bound carbonic

acid. This result was the average of ten closely agreeing determinations on this solution; and the figures for the carbonic acid found, when magnesium was present, should be compared with it.

TABLE SHOWING EFFECT OF NON-PRECIPITATION OF MAGNESIUM HYDROXIDE IN DETERMINATIONS OF CARBONIC ACID BY TRILLICH'S METHOD.

MgO added; equiv. to CO_2. Parts per million.	Ba_2OH_2 solution. N/20 (approx.). cc.	CO_2 found by titration. Uncorr. Parts per million.	Theoretical correction for MgO. Parts per million.	CO_2 corrected for MgO. Parts per million.	MgO equiv. to parts per million CO_2 Ppt'd. Parts per million.	MgO equiv. to parts per million CO_2 Not ppt'd. Parts per million.
10	10	49.5	10	39.5	3.3	6.7
10	10	50.6	10	40.6	4.4	5.6
10	10	49.4	10	39.4	3.2	6.8
10	10	49.4	10	39.4	3.2	6.8
10	10	49.4	10	39.4	3.2	6.8
20	15	59.2	20	39.2	13.0	7.0
20	15	57.9	20	37.9	11.7	8.3
20	15	57.9	20	37.9	11.7	8.3
20	15	57.9	20	37.9	11.7	8.3
20	15	57.9	20	37.9	11.7	8.3
30	15	64.6	30	34.6	18.4	11.6
30	15	63.4	30	33.4	17.2	12.8
30	15	64.6	30	34.6	18.4	11.6
50	20	83.0	50	33.0	36.8	13.2
50	20	81.6	50	31.6	35.4	14.6
50	20	83.0	50	33.0	36.8	13.2

Note.—Amount of magnesium oxide actually present is equal to 10/11 of amounts given as "MgO equivalent to parts per million of CO_2."

The results given above of course exaggerate the error because of the small amount of barium hydroxide and the large amounts of magnesium. They serve to show, however, the error which might arise from this source.

The errors affecting the accuracy of Pettenkofer's and Trillich's methods may be briefly summed up as follows:

1. The error due to the carbonating of the barium hydroxide as a result of manipulation. This is common to both methods and tends to make results higher than they should be. With careful work it can be kept very low and ought not to exceed 1 or 2 parts per million.

2. In Pettenkofer's method the solution of the carbonates by ammonium chloride, which tends to lower the results, seems to be the source of greatest error. The magnitude of this error appears to be governed by the concentration of the barium hydroxide solution and the amount of ammonium chloride present.

3. In the Trillich method the non-precipitation of the magnesium salts, as magnesium hydroxide, tends to lower the results. The excess of barium hydroxide over and above that necessary for the reaction, appears to be fully as necessary here as in Pettenkofer's method. It is probably best to have at least an excess of from 30 to 35 cc. of 0.05 normal barium hydroxide solution for waters containing as much as 60 parts per million of magnesium oxide. The magnitude of this error may vary (even when the prescribed amount of 45 cc. of an approximately 0.05 normal barium hydroxide solution is added to each 100 cc. of water), from 2 to 5 parts per million. This amount may be exceeded with an insufficient excess of barium hydroxide.

Since the error due to unavoidable carbonating of the barium hydroxide in the course of manipulation, increases the results, and all errors arising from solubility of carbonates or non-precipitation of magnesium hydroxide lowers them, these errors tend to neutralize each other. But if the error of manipulation is kept at a minimum, the lowering of the results due to other causes, exceeds the increase, and in consequence too low results are obtained.

LUNGE-TRILLICH OR SEYLER METHOD.

This method depends on the action of phenolphthalein as an indicator in the presence of free carbonic acid and of carbonates and bicarbonates of the alkaline earth bases; and on the assumption that in the bicarbonates of these bases there is one molecule of half-bound carbon dioxide for each molecule of fixed carbon dioxide.

Leeds[1] in this country and Trillich in Europe proposed, at about the same time, the determination of the free carbonic acid in water by titrating the sample with a solution of sodium carbonate, using phenolphthalein as the indicator. The sodium carbonate reacts with the free carbonic acid to form sodium bicarbonate. As soon as the free acid is neutralized, any further addition of sodium carbonate produces a pink color. This affords a direct means for estimating the free carbonic acid without involving the half-bound. With waters which are acid to phenolphthalein, the determination of the fixed carbonic acid by Hehner's method gives at once the half-bound carbonic acid according to

[1] This Journal, **13**, 95 (1891).

the assumption stated in the preceding paragraph. With waters which are alkaline to phenolphthalein, by the determination of this "phenolphthalein alkalinity" and the "total alkalinity" obtained with lacmoid as the indicator, the amount of half-bound carbonic acid can easily be estimated. In the latter case of course free carbonic acid is absent.

Seyler, who has made a study of this method, considers it one which gives accurate results, and one which is free from many of the difficulties involved in Pettenkofer's and Trillich's methods. The chief criticism of the method seems to have been as to the correctness of the assumption for quantitative purposes, that, when a water was acid or neutral to phenolphthalein, there was present for each molecule of fixed carbonic acid, one molecule of half-bound carbonic acid; and to the claim that when the water was alkaline to phenolphthalein, only one-half the carbonic acid in the form of the normal carbonates was determined by titrating with acid to the discharge of the color produced by this indicator.

If to 10 cc. of a cold 0.02 normal solution of sodium carbonate, phenolphthalein be added, and then a 0.02 normal solution of sulphuric acid, it will be found that only 5 cc. of the latter are required to discharge the color. The reaction is as follows:

$$2Na_2CO_3 + H_2SO_4 = 2NaHCO_3 + Na_2SO_4.$$

The pink color produced by the phenolphthalein in the sodium carbonate solution is destroyed when one-half the latter becomes saturated with the carbonic acid liberated by the mineral acid; and this occurs when one-half the base has been neutralized. It is therefore evident that bicarbonates of the fixed alkalies are neutral to phenolphthalein.

The assumption that carbonates of the alkaline earth bases react in an analogous manner, is, so far as we can ascertain, correct, as the following experiments will show.

A calcium bicarbonate solution was boiled down to about one-third or one-fourth of its original volume and allowed to cool out of contact with the air. The precipitated calcium carbonate settled out, only such remaining in solution as was soluble without the presence of any free or half-bound carbonic acid. Several portions of the supernatant liquid were withdrawn and titrated with acid, using phenolphthalein as the indicator. The total alkalinity of the solution was also determined with the indicator lacmoid.

ACTION OF PHENOLPHTHALEIN AS AN INDICATOR IN A SOLUTION OF CALCIUM CARBONATE.

No.	Calcium carbonate solution.	Sulphuric acid. N 50 (approx.). A.[1]	Sulphuric acid. N 50 (approx.). B.[2]
	cc.	cc.	cc.
1	100	1.65	3.15
2	100	1.65	3.25
3	100	1.50	3.10
	Average,	1.60	3.17

A solution of magnesium carbonate acted similarly, 1.65 cc. of acid being required to discharge the pink color formed with phenolphthalein, and 3.4 cc. to obtain the end-point with lacmoid. The reaction involved in these two cases is doubtless analogous to the one which takes place in sodium carbonate solutions; *viz.*,

$$2CaCO_3 + H_2SO_4 = Ca(HCO_3)_2 + CaSO_4.$$

It was found that these solutions of calcium and magnesium carbonate were very sensitive to the absorption of carbon dioxide from the air, even on a very short exposure; and also that it was extremely difficult to free them from the last traces of the half-bound carbonic acid. Only by violent and prolonged boiling and cooling out of contact with the air, could this be accomplished. A calcium carbonate solution, which after boiling was cooled in air free from carbon dioxide, required for 100 cc., 1.5 cc. of acid with phenolphthalein as the indicator, and 3.1 cc. with lacmoid. A portion of the same liquid cooled in a beaker, required 0.95 cc. of acid with phenolphthalein and 3.2 cc. with lacmoid. Magnesium carbonate solutions absorbed carbon dioxide more slowly, as has been previously pointed out.

Hot solutions of calcium carbonate and of magnesium carbonate do not react to phenolphthalein in the same manner as do these cold solutions, since in the former the bicarbonates formed by the liberation of the carbonic acid from the normal carbonates, are immediately decomposed by the heat with evolution of carbon dioxide. It is therefore possible to determine the whole of the carbonates of the alkaline earth bases even with phenolphthalein as the indicator, provided the solution is kept boiling. The same is true of the carbonates of sodium and potassium. But phenolphthalein is by no means a good indicator for this purpose and the results are much more accurately obtained with lacmoid or one of a similar character.

[1] To discharge pink color with phenolphthalein.

[2] To obtain end-point with lacmoid.

It has been considered probable that sodium carbonate in solution undergoes hydrolysis in the following manner.

$$Na_2CO_3 + H_2O = NaHCO_3 + NaOH.$$

As the sodium bicarbonate thus formed supplies no hydrogen ions, and the sodium hydroxide is dissociated producing a large number of hydroxyl ions, the solution is therefore quite strongly alkaline. To phenolphthalein it exhibits the alkalinity characteristic of caustic alkaline solutions. It may be that a similar hydrolysis takes place in the case of calcium carbonate and magnesium carbonate solutions.

$$2CaCO_3 + 2H_2O = Ca(HCO_3)_2 + Ca(OH)_2.$$

If this does occur it readily explains why calcium and magnesium carbonate solutions are alkaline to phenolphthalein and why they show the same evidence of the presence of hydroxyl ions as in the case of sodium carbonate solutions.

The essential details of the Seyler process are as follows:

The free carbonic acid is determined by placing 100 cc. of the sample in a glass cylinder with 25 to 30 drops of a neutral solution of phenolphthalein. To the sample is then added a solution of sodium carbonate (0.05 or 0.02 normal solution may be used), stirring carefully and thoroughly until a faint permanent pink color is obtained.

The following precautions have been found desirable if accurate results are to be expected.

1. The titration can conveniently take place in a short Nessler cylinder. The writers used a tube approximately 18 cm. long by 3 cm. in diameter, graduated for 50 and 100 cc. The stirring rod used was bent at its lower end into the form of a circle and then turned so as to stand at right angles to the rod. A comparison cylinder containing the same amount of water as there was in the titrating cylinder, was found to aid in the determination of the end-point.

2. The larger part of the sodium carbonate solution should be added quickly and the strong pink color formed should be discharged by stirring and mixing with the rod. The titration can then be cautiously completed. When the color remains permanent the titration is complete. The sodium carbonate solution should be prepared with freshly ignited sodium carbonate and with water which has been thoroughly boiled and cooled out of

contact with the air. The exposure of this solution to the air should be avoided as much as possible as sodium bicarbonate is readily formed, which renders it useless for this titration where accurate results are desired.

3. With waters that are high in free and half-bound carbonic acid it is better to use less than 100 cc. for the titration, especially if 0.02 normal sodium carbonate solutions are used. With such a water, care is necessary in transferring the sample to the cylinder in order to avoid loss of carbonic acid. Too vigorous stirring of the water is also to be avoided for the same reason.

The fixed carbonic acid, from which the half-bound acid is estimated, is determined according to the method of Hehner. Seyler uses methyl orange as the indicator for this titration, but the writers employed lacmoid. The accuracy of this process[1] is well-known and need not be here discussed.

In the absence of free carbonic acid in a water, the half-bound may equal the fixed, in which case it would be neutral to phenolphthalein. If, however, the water is alkaline to phenolphthalein, the half-bound carbonic acid does not equal the fixed ; or in other words a portion of the carbonates of the bases exist in solution without the assistance of any half-bound carbonic acid. In such a case the half-bound acid is obtained by first determining the fixed carbonic acid by means of lacmoid. From this is deducted an amount of carbonic acid equal to twice the quantity indicated by the acid required to discharge the pink color produced by phenolphthalein. The difference is the amount of half-bound carbonic acid which is present. These titrations may be made on the same sample, in which case the "phenolphthalein alkalinity" is first determined and then followed by the titration with lacmoid ; or they may be made on separate samples.

The principles on which the above procedure is based have been pointed out above.

These titrations involve no especial difficulties and can be easily and quickly carried out. Approximately 0.02 normal solutions of sulphuric acid were used by the writers and the same strength of sodium carbonate solution. Seyler has prepared a series of formulas for calculating the results, which simplifies the work somewhat. If results are obtained with 100 cc. of the sample

[1] J. W. Ellms : This Journal, **21**, 359.

and the reagents employed are 0.02 normal the following formulas express the results in parts per million.

I. For waters acid or neutral to phenolphthalein :

Free carbonic acid	$= 4.4p$
Fixed or half-bound carbonic acid	$= 4.4m$
Volatile carbonic acid	$= 4.4(m - p)$
Total " "	$= 4.4(2m - p)$

p = cc. 0.02 normal sodium carbonate solution required to produce a pink color with phenolphthalein in 100 cc. of the water ; and

m = cc. 0.02 normal sulphuric acid solution required to obtain the end-point with methyl orange or lacmoid in the same volume of water.

II. For waters alkaline to phenolphthalein :

Fixed carbonic acid	$= 4.4\ m$
Half-bound or volatile carbonic acid	$= 4.4(m - 2p')$
Total carbonic acid	$= 4.4(2m - 2p')$

m = cc. 0.02 normal sulphuric acid solution required to obtain end-point with methyl orange or lacmoid in 100 cc. of the sample.

p' = cc. 0.02 normal sulphuric acid required to discharge the pink color produced by phenolphthalein in 100 cc. of the sample.

There is a third case in which free carbonic acid might exist in a solution containing free mineral acid and for which Seyler has given a method with its corresponding formulas for calculating the results. But such a condition would seldom be found in natural waters and need not here be described.

The errors affecting the accuracy of Seyler's method are those which arise in part from the determination of the free carbonic acid. The end-point in the titration of the sample with sodium carbonate and phenolphthalein is not entirely satisfactory. The results obtained are usually low, but with care and practice the error from this source should be less than 2 to 3 parts per million, even with considerable amounts of carbonic acid, and on small amounts it is less still.

The error due to the determination of the fixed carbonic acid, from which the half-bound is derived, arises from those errors involved in the carrying out of Hehner's method and which in good work ought not to exceed 1 to 2 parts per million.

COMPARISON OF THE THREE METHODS ON WATERS CONTAINING KNOWN AND UNKNOWN AMOUNTS OF CARBONIC ACID.

The comparison of the results obtained with known solutions of carbonic acid indicate the relative and actual accuracy of these three methods. Solutions containing known amounts of free and half-bound carbonic acid were prepared by neutralizing partially or wholly measured quantities of a 0.02 normal solution of sodium carbonate with a 0.02 normal solution of sulphuric acid. Solutions of calcium and magnesium salts were introduced in order that these bases might be present and thus produce an artificial water having approximately the same composition as natural waters.

The first table shows the amount of free carbonic acid obtained in a solution known to contain 44 parts per million. This solution contained no calcium or magnesium salts. The term "Trillich method" has been used in the column headings of the following tables in the sense in which it was defined in the first portion of this paper. Strictly speaking, in the absence of magnesium salts where the use of ammonium chloride is unnecessary, the columns could have been headed "Pettenkofer method;" but to avoid confusion the definitions first given have been adhered to.

TABLE SHOWING FREE CARBONIC ACID FOUND IN A SOLUTION KNOWN TO CONTAIN 44 PARTS PER MILLION.

No.	Trillich method. Parts per million.	Seyler method. Parts per million.
1	41.7	44.2
2	43.7	44.7
3	42.2	44.2
4	40.8	43.8
5	42.7	44.0
6	41.7	43.6
7	40.8	44.4
Average,	42.0	44.0

When free and half-bound carbonic acid were present together in known amounts the following results were obtained:

TABLE SHOWING FREE AND HALF-BOUND CARBONIC ACID FOUND IN A SOLUTION KNOWN TO CONTAIN 8 PARTS FREE AND 40 PARTS HALF-BOUND CARBONIC ACID. (FREE AND HALF-BOUND ACID EQUALS 48 PARTS PER MILLION.)

No.	Trillich method. Free and half-bound acid. Parts per million.	Seyler method. Free acid. Parts per million.	Seyler method. Half-bound acid. Parts per million.	Seyler method. Free and half-bound acid. Parts per million.
1	47.0	7.0	40.8	47.8
2	46.1	6.2	41.3	47.5
3	46.1	6.6	41.3	47.9
4	47.0	7.0	41.3	48.3
5	47.0	7.9	41.3	49.2
6	45.0	7.9	41.3	49.2
7	45.4	7.5	41.3	48.8
8	46.1	7.9	40.8	48.7
9	46.1	7.0	41.3	48.3
10	46.1	7.9	41.3	49.2
Average,	46.2	7.3	41.2	48.5

The following table shows the results obtained with these methods, when the solution contained double the amount of free and half-bound carbonic acid as was present in the solution from which the figures in the preceding table were obtained.

TABLE SHOWING FREE AND HALF-BOUND CARBONIC ACID FOUND IN A SOLUTION KNOWN TO CONTAIN 16 PARTS FREE AND 80 PARTS HALF-BOUND CARBONIC ACID. (FREE AND HALF-BOUND ACID EQUALS 96 PARTS PER MILLION.)

No.	Trillich method. Free and half-bound acid. Parts per million.	Seyler method. Free acid. Parts per million.	Seyler method. Half-bound acid. Parts per million.	Seyler method. Free and half-bound acid. Parts per million.
1	92.2	15.8	78.2	94.0
2	91.0	14.5	81.1	95.6
3	91.0	14.1	81.1	95.2
4	90.5	14.5	80.2	95.2
5	90.5	15.0	80.2	94.7
Average,	91.0	14.8	80.1	94.9

No attempt has been made in our work with Pettenkofer's and Trillich's methods to differentiate by titration (according to Trillich's method), the free carbonic acid from the half-bound. Assuming, however, that the half-bound acid in the above solution is, as shown by the average, 80.1 parts per million, then the free carbonic acid by Pettenkofer's or Trillich's method would be 91 parts minus 80.1 parts or 10.9 parts per million.

In the following table are shown comparisons made with solutions containing known amounts of free and half-bound carbonic acid, and which also contained varying but known amounts of magnesium salts.

TABLE SHOWING FREE AND HALF-BOUND CARBONIC ACID FOUND IN SOLUTIONS KNOWN TO CONTAIN 4.9 PARTS FREE AND 41.6 PARTS PER MILLION OF HALF-BOUND CARBONIC ACID, AND WITH VARYING AMOUNTS OF MAGNESIUM SULPHATE. (FREE AND HALF-BOUND ACID EQUALS 46.5 PARTS PER MILLION.)

No.	Magnesium sulphate present equivalent to carbonic acid. Parts per million.	Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method. Free carbonic acid. Parts per million.	Seyler method. Half-bound carbonic acid. Parts per million.	Seyler method. Free and half-bound carbonic acid. Parts per million.
1	10	44.6	43.9	4.6	48.2	45.8
2	10	43.1	43.9	...	....	....
3	10	43.1	44.4	...	....	....
4	20	41.5	45.6	4.3	41.2	45.5
5	20	44.6	44.2	4.0	41.9	45.9
6	40	44.6	43.3	4.0	42.6	46.6
7	40	43.1	40.4	4.6	41.2	45.8
8	40	46.0	40.4	...	....	....
	Average,	43.8	43.2	4.3	41.6	45.9

Assuming as in the preceding tables that the half-bound carbonic acid is on an average 41.6 parts per million in the above solution, then the Pettenkofer results indicate 2.2 parts per million of free carbonic acid and the Trillich results 1.6 parts per million.

Comparisons were also made on natural waters containing unknown amounts of free and half-bound carbonic acid. The first table given below shows the results obtained on a sample of Ohio river water by the three different methods. This sample of water contained by a gravimetric determination 10 parts per million of magnesium oxide equivalent to a correction to be applied to the Trillich figures of 11 parts per million.

TABLE SHOWING AMOUNT OF CARBONIC ACID FOUND IN OHIO RIVER WATER BY THE THREE METHODS.

No.	Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method. Free carbonic acid. Parts per million.	Seyler method. Half-bound carbonic acid. Parts per million.	Seyler method. Free and half-bound carbonic acid. Parts per million.
1	14.9	15.4	0.6	16.2	16.8
2	14.9	16.8	0.4	16.4	16.8

No.	Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method. Free carbonic acid. Parts per million.	Seyler method. Half-bound carbonic acid. Parts per million.	Seyler method. Free and half-bound carbonic acid. Parts per million.
3	13.4	16.1	0.4	16.2	16.6
4	14.4	16.8	0.4	16.6	17.0
5	14.4	16.8	0.6	16.6	17.2
6	14.4	16.1	0.6	16.2	16.8
7	13.4	16.8	0.4	16.4	16.8
8	14.9	15.4	0.4	16.6	17.0
9	13.2	16.8	0.4	16.6	17.0
Average,	14.2	16.3	0.4	16.4	16.8

The following well water was also examined and is given as an illustration of a water highly charged with carbonic acid and containing a large quantity of mineral salts, especially those of magnesium. A gravimetric determination of the calcium and magnesium, and also of the sulphuric acid, gave the following results.

WELL WATER.

	Parts per million.
Lime (CaO)	378
Magnesia (MgO)	128
Sulphuric acid (SO_3)	351

The free and half-bound carbonic acid were determined by the three volumetric methods and the results obtained are shown in the following table:

TABLE SHOWING AMOUNT OF CARBONIC ACID FOUND IN A WELL WATER BY THE THREE METHODS.

No.	Pettenkofer method. Free and half-bound carbonic acid. Parts per million.	Trillich method. Free and half-bound carbonic acid. Parts per million.	Seyler method. Free carbonic acid. Parts per million.	Seyler method. Half-bound carbonic acid. Parts per million.	Seyler method. Free and half-bound carbonic acid. Parts per million.
1	241	242.4	63.4	176.4	239.8
2	241	236.5	66.9	176.4	243.3
3	241	236.5	68.6	176.4	245.0
4	241	246.3	65.1	177.4	242.5
5	238	242.4	68.6	176.4	245.0
Average,	240.4	240.8	66.5	176.6	243.1

As would be expected the variation in the above results is in some cases considerable, but the greatest difference is less than 10 parts per million and the greatest variation from the mean of all the results is less than 5 parts per million.

The results of the above analysis were all obtained on waters which when cold reacted neutral or acid to phenolphthalein. There is one other class of waters, which when cold react alkaline to phenolphthalein, and which in consequence require a modification of Seyler's method as previously described. The number of waters belonging to this class does not seem to be at all large, and the writers have never examined but one water which showed this feature. Seyler states that pure sea water is alkaline to phenolphthalein. He gives the following analysis:

	Parts per million.
Free carbonic acid	0
Half-bound carbonic acid	44.0
Fixed carbonic acid	51.7
Total carbonic acid	95.7

He also states that he has found well waters which upon standing exposed to the air for some time, reacted alkaline to phenolphthalein, and that such waters contained considerable magnesium carbonate.

The writers have found that at certain times the Mississippi river water is alkaline to phenolphthalein. How long such periods last or at what seasons of the year they occur, we have not had the opportunity to determine. It is quite probable that the so-called "alkali waters" of the Western plains would react alkaline to phenolphthalein as they contain carbonates of sodium. It has been noted that water which has stood in the iron pipes of the laboratory for some time, will, when first drawn, react alkaline to phenolphthalein. This is due probably to the free carbonic acid and bicarbonates in the water reacting with the iron of the pipe to form carbonate of iron, and thus leaving in solution small amounts of normal calcium and magnesium carbonates.

The water examined by us, which reacted alkaline to phenolphthalein, was a mixed sample of Mississippi river water. The samples were taken during the month of September, 1900, opposite Quincy, Illinois. When examined it was found to give a strong pink color with phenolphthalein. Its average approximate composition was as follows:

	Parts per million.	
Lime (CaO)	35.6	equivalent to 63.5 parts $CaCO_3$.
Magnesia (MgO)	16.0	" " 33.6 " $MgCO_3$.
Sulphuric acid (SO_3)	7.2	
Chlorine (Cl)	6.3	
Fixed carbonic acid (CO_2)	39.8	" " 90.4 " when expressed in the form of calcium carbonate.

From a consideration of these results it is more than probable that the magnesium was present partly as normal magnesium carbonate ($MgCO_3$), and the calcium as calcium bicarbonate. Only a limited quantity of the sample was available for experimental purposes. The following table shows the average of the results obtained in determining the carbonic acid by the three volumetric methods.

CARBONIC ACID OBTAINED IN A SAMPLE OF MISSISSIPPI RIVER WATER.

Pettenkofer method.		Trillich method.		Seyler method.	
Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.
0	0	0	34.6	0	35.4

Seven different portions of this water treated according to Pettenkofer's method showed that in no instance was any barium hydroxide used up, and that on an average only 60 parts per million (expressed in terms of $CaCO_3$) of carbonates were precipitated out, which still left in solution about 30 parts per million. The reason for this is not clear, but it is probable that the ammonium chloride used was one factor which was instrumental in holding a portion of the carbonates in solution. Whether the dissolved organic matter, which was in considerable amount, was another cause of such unusual results, we are unable to state.

An artificial water prepared so as to contain approximately the same amounts of calcium and magnesium carbonates as were present in the Mississippi river sample, gave the following results:

	Pettenkofer method.		Trillich method.		Seyler method.	
No.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.	Free carbonic acid. Parts per million.	Half-bound carbonic acid. Parts per million.
1	0	27.9	0	31.6	0	31.7
2	0	29.4	0	31.6	0	32.2
Average,	0	28.6	0	31.6	0	31.9

This water contained 11 parts per million of magnesium oxide, equivalent to a correction in the Trillich method of 12 parts per million.

The tendency here is for Pettenkofer's method to give low results, but the carbonates are not affected to the extent that they were in the river water.

CONCLUSIONS.

From a consideration of the data obtained in this investigation, it appears that the Lunge-Trillich or Seyler method is the most accurate of the three volumetric methods. The "free and half-bound carbonic acid" as determined on known amounts by this method is on an average less than 1 per cent. too low and shows a possible range of less than $\pm$ 3 per cent. The accuracy of the determination of the "free carbonic acid" is somewhat less, and although the percentage error for low amounts is rather high, the variation from the actual amount is not more than 2 to 3 parts per million. These results are always too low and introduce into the determination of the "volatile carbonic acid" the larger proportion of the error.

Trillich's modification of Pettenkofer's method is less accurate than the Seyler method but more accurate than the Pettenkofer. Results obtained with either Pettenkofer's or Trillich's method are almost always too low. They probably give figures which are on an average between 5 and 10 per cent. too low. While Trillich's method gives more uniform results than Pettenkofer's the figures appear to be about 5 per cent. too low, and they may be as much as 10 or 12 per cent. too low.

Pettenkofer's method is inclined to give still lower results and although those obtained seemed to be only from 1 to 2 per cent. lower than those obtained with Trillich's method, yet it appears somewhat unreliable and one in which under some conditions extremely erratic results are likely to occur. With very low amounts of carbonic acid the percentage error in both Pettenkofer's and Trillich's methods are much greater than those stated above, although it may only represent an actual difference of from 3 to 4 parts per million.

For ease and rapidity of manipulation, for avoidance of difficulties arising from the presence of magnesium salts, and for its greater accuracy, the Lunge-Trillich or Seyler method is, in the opinion of the writers, to be preferred to either of the other two volumetric methods.

LABORATORY "COMMISSIONERS OF WATER WORKS,"
CINCINNATI, OHIO.

NOTES.

Notes on the Paper by Hiltner and Thatcher.[1]—The method proposed in the paper is a modification of the Sachs-Le Docte modification of Pellet's "instantaneous aqueous diffusion method."[2] The device of weighing any convenient quantity of pulp and adding thereto the proper proportionate quantity of a mixture of water and lead acetate solution, first suggested by Walawski in 1894, has been practiced in this laboratory for the two seasons past. In 1899, or earlier, a special burette was obtained, the same being made to order for the purpose, after a drawing and description devised and wrought by Dr. G. L. Spencer.

The ideas contained in the paper that are new, other than those mentioned above, seem to be principally in regard to the allowance to be made for the liquid matter in the beet pulp, and the means of determining the amount of allowance to be made. It seems that the authors of the paper are in error :

First, because they base their corrections on the percentage of water in the beet, instead of on the percentage of liquid (juice) in the beet. The substances (sugar, etc.) dissolved in the water contained in the beet must necessarily increase the volume of that water as calculated from its weight at a given temperature. (See p. 309).

Second, because their determinations of water contained in beets, as reported on pages 308 and 309 are higher than is indicated by previous results of determinations of the amount of fiber contained in beets. For example, if in Table I we make the following additions, we obtain totals that are too high.

	Per cent.	Per cent.	Per cent.	Per cent.
Average water	84.64	83.05	82.10	81.25
Average sugar	9.00	11.00	13.00	14.00
Average non-sugar (calculated)	2.25	1.94	2.29	2.47
Total.....	95.89	95.99	97.39	97.72
Difference (marc).....	4.11	4.01	2.61	2.28

The non-sugar is here obtained by calculation from the percentage of sugar, assuming a purity coefficient of 80 in the first

[1] See this Journal, **23**, 299.

[2] See Spencer's "Handbook for Beet-Sugar Chemists," p. 181.

case and 85 in the other three cases. As little as 4 per cent. of marc is possible, but 2.61 per cent. is doubtful, and 2.28 per cent. still more so. Making the same calculations from data given in Table II, we obtain:

	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Average water.....	81.74	82.00	84.51	83.27	81.89	81.21
Average sugar.....	12.70	11.90	8.60	11.80	12.30	13.60
Average non-sugar...	3.18	2.98	2.15	2.95	3.08	3.40
Total....	97.62	96.88	95.26	98.02	97.27	98.21
Difference (marc)....	2.38	3.12	4.74	1.98	2.73	1.79

The percentages of non-sugar given in this table are calculated, assuming a purity of 80 for the juices of the beets.

From the data obtained in these two tables, the authors conclude: "All of these figures indicate that for beets, most of which contain between 8 per cent. and 14 per cent. of sugar, 83 per cent. might be assumed as an average water factor without there being a variation in any individual case of more than 3 per cent."

In the case of pulp having 83 per cent. of water, 26.048 grams of it contain 21.62 grams of water measuring 21.62 Mohr's cc. at 17.5° C. Assuming a purity coefficient of 80, a beet containing 8 per cent. of sugar would contain 10 per cent. of soluble solids, while one containing 14 per cent. of sugar would contain 17.5 per cent. of soluble solids. If a solution be prepared for analysis by mixing 26.048 grams of pulp with 78.38 Mohr's cc. of water measured at 17.5° C., we would have in the two cases:

	Beets containing 8 per cent. sugar. Grams.	Beets containing 14 per cent. sugar. Grams.
Water in pulp.....	21.62	21.62
Soluble solids in pulp.....	2.6048	4.5584
Water added.....	78.38	78.38
Total....	102.6048	104.5584
Percentage of soluble solids in the mixture.....	2.54	4.36
Specific gravity of the liquid in the mixture.....	1.00992	1.01714
Volume of the liquid in the mixture, Mohr's cc. at 17.5° C	101.60	102.80

Working by this method, therefore, the volume of the solution would be 1.6 to 2.8 per cent. too great under the conditions of these two examples. The soluble solids materially increase the volume of the solution.

The ordinary manner of arriving at the allowance to be made in analyses by this method is to assume an average juice content

for the beets, and allow for the volume of the assumed quantity of juice of average density.

In the case of beets containing 95 per cent. of juice, 26.048 grams of pulp contain 24.7456 grams of juice, or 23.60 cc. when the juice is 12° Brix, and 22.84 cc. when the juice is 20° Brix.

In case of 90 per cent. juice, 26.048 grams of pulp contain 23.4432 grams of juice; or 22.36 cc. and 21.64 cc. of liquid in the cases of 12° Brix and 20° Brix juice respectively. Assembling these data in the form of a table we have:

VOLUME OF JUICE CONTAINED IN 26.048 GRAMS OF PULP.

	12° Brix. cc.	20° Brix. cc.	Means. cc.
95 per cent. juice	23.60	22.84	23.22
90 per cent. juice	22.36	21.64	22.00
Means	22.98	22.24	22.61

A quantity of liquid of 16° Brix that measures 22.61 cc. at 17.5° C. weighs 24.0944 grams and contains 3.8550 grams of solids. 23.6 cc. of liquid, 12° Brix, weigh 24.7456 grams and contain 2.9694 grams of solids. 21.64 cc. of liquid, 20° Brix, weigh 23.4432 grams and contain 4.6886 grams of solids.

If 26.048 grams of beet pulp of the qualities just described be mixed at 17.5° C. with water equivalent to 100 cc., less the volume of liquid contained in the pulp, mixtures of the following compositions and properties will be obtained:

	Beets containing 95 per cent. of juice of 12° Brix.	Beets containing 90 per cent. of juice of 20° Brix.	Beets containing 92.5 per cent. of juice of 16° Brix.
	Grams.	Grams.	Grams.
Water contained in pulp	21.7762	18.7546	20.2394
Added water	76.40	78.36	77.39
Soluble solids in pulp	2.9694	4.6886	3.8550
Total	101.1456	101.8032	101.4844
Percentage of soluble solids in the mixture	2.94	4.61	3.80
Specific gravity of the liquid in the mixture	1.0115	1.01814	1.01491
Volume of the liquid in the mixture, Mohr's cc. at 17.5° C.	99.996	99.989	99.993

The quantities of water added in the first two cases, vary

approximately 1 cc. from the last mean case. If we use 77 cc. in each case as directed by the Sachs-Le Docte method, irrespective of the quality of the beets, we have errors as follows in two extreme cases:

	Beets containing 95 per cent. of juice of 20° Brix. Grams.	Beets containing 90 per cent. of juice of 12° Brix. Grams.
Water contained in pulp	19.7965	20.6300
Water added (Sachs-Le Docte)	77.0000	77.0000
Soluble solids in pulp	4.9491	2.8132
Total	101.7456	100.4432
Percentage of soluble solids in the mixture	4.86	2.80
Specific gravity of the liquid in the mixture	1.01914	1.01094
Volume of liquid in the mixture in Mohr's cc. at 17.5° C	99.83	99.35

If we take the other two extremes, we have for

	Beets containing 95 per cent. of juice of 12° Brix. Grams.	Beets containing 90 per cent. of juice of 20° Brix. Grams.
Water contained in pulp	21.7762	18.7546
Water added (Sachs-Le-Docte)	77.0000	77.0000
Soluble solids in pulp	2.9694	4.6886
Total	101.7456	100.4432
Percentage of soluble solids in the mixture	2.92	4.67
Specific gravity of the liquid in the mixture	1.01142	1.01838
Volume of the liquid in the mixture in Mohr's cc. at 17.5° C	100.60	98.63

In these extreme cases the error varies from 0.17 cc. to 1.37 cc.; or rather, from 0.6 cc., too great a volume, to 1.37 cc., too small a volume. The increase of the volume of the water contained in the pulp, due to matter dissolved in it, is not appreciably lessened when the liquid is diluted to 100 cc. It therefore seems that the error attending the use of the Sachs-Le Docte allowance of 23 cc. for the liquid contained in the pulp will not be greater than that attending the method of Hiltner and Thatcher. This is especially true when 26.048 grams of pulp are mixed with 177 cc. of water instead of 77 cc.

In the case of beets that are both very rich and very dry because of their conditions of growth or storage, the proportion of water to be added to a given weight of pulp should undoubtedly be increased.

The balance mentioned on page 314 I believe to be the "Steinke Matador, Pracisionswaage ohne Benutzung von Gewichten." We have tried this balance in this laboratory for the purpose mentioned and have found it to be wholly inaccurate and useless for this purpose.

On page 309, the authors of the paper are led to make an unjust criticism of the method proposed by Walawski, because of a typographical error made by us in the translation of Sachs' paper. Walawski recommended the addition of a weight of water equal to 3 times the weight of the pulp and not 3.6 times the weight of the pulp as stated.

In the closing paragraphs of their paper, the authors describe an application of their method to the analysis of beet juices, which needs a word of comment.

They state that "A water factor of 85 per cent. was adopted." This implies that the beet juices were assumed to contain 15 per cent. of total solids, which corresponds to a specific gravity of 1.06133. 26.048 grams of juice of this density measure 24.54 Mohr's cc. at 17.5° C. At 30° C. the specific gravity would be somewhat less; the volume would be approximately 24.63 Mohr's cc. It is difficult to understand how the excellent comparative results would have been obtained by the authors of this paper by allowing only 22.14 cc. for the increase in the volume of the mixture due to the beet juice.

E. E. EWELL.

DIVISION OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C.,
March 20, 1901.

NEW BOOKS.

THE TESTING AND VALUATION OF RAW MATERIALS USED IN PAINT AND COLOUR MANUFACTURE. By M. W. JONES, F.C.S. A book for the laboratories of colour works. 88 pages. Price, $2.00.

Excepting a chapter on oils, this book is devoted to a general survey of the most important inorganic raw materials used by the trade. The subjects treated under separate headings are: China clay, ammonium hydrate, acids, ultramarine, oils, and the compounds of aluminium, iron, potassium, sodium, chromium, tin, copper, lead, zinc, manganese, arsenic, antimony, calcium, barium, cadmium, mercury, cobalt, and carbon.

Suitable tests are given for the detection of impurities and adulterants; and the schemes of analysis are familiar ones, simple,

accurate, and precisely described. Gravimetric methods are given in nearly every case supplemented in many instances by volumetric. The chapter on oils is confined to the estimation of fatty acids in Turkey-red oil, and to the detection in linseed oil of mineral, resin, raw or boiled oils.

The book is an excellent compilation which will undoubtedly find favor in the laboratory. It has an index.

C. W. PARMELEE.

CHRISTIAN FRIEDRICH SCHÖNBEIN, 1799-1868. Ein Blatt zur Geschichte des 19. Jahrhunderts, von GEORG W. A. KAHLBAUM und ED. SCHAER. 2 vols., Leipzig, 1899-1901. Vol. I, 230 pp. Portrait; Vol. II, 326 pp. (Viertes und sechtes Hefte Monographien aus der Geschichte der Chemie, herausgegeben von Georg W. A. Kahlbaum.)

These two volumes contain the life history of that remarkable man who will always be remembered as the discoverer of four notable things of diverse nature in their physical and chemical aspects, the Passivity of Iron, Ozone, Guncotton and Collodion.

The author, who occupies the chair of chemistry in the University of Basle, has enjoyed the best opportunities for gathering the data needed for his work; from the three living daughters of Schönbein, from his friends both in Germany and in England, he has had for study not less than 1600 letters, and through libraries and personal friends he has consulted 350 of Schönbein's printed papers. And with these aids he has portrayed the man in his scientific pursuits and social life.

Schönbein, who was born 18th October, 1799, in what is now known as the kingdom of Würtemberg, inherited a love for chemistry from his father, who was a dyer and as such occupied with problems requiring chemical knowledge. At the age of twenty-one he entered the manufactory of chemicals of Dr. J. G. Dingler, in Augsburg, where his daily labor extended from 6 A.M. to 7 P.M., leaving him only from 4 to 6 A.M. and from 7 to 10 P.M. for private study and recreation. For this he received board and lodging and 200 to 300 florins a year. Dingler had just begun to publish his *Polytechnisches Journal.* (1820–1901).

After studying some semesters at the Universities of Tübingen and Erlangen, he secured a position as teacher of physics, chemistry, and mineralogy in the educational institution founded a few years before by Friedrich Fröbel, of kindergarten fame. In 1826 we find him a teacher in London, and in 1828 again on the con-

tinent, teaching experimental chemistry at the University of Basle, where he was made professor of chemistry and physics in 1835.

We cannot in a book-review further follow his fortunes in such detail; suffice it to say that he made all his notable discoveries after he had reached the age of 36, and while holding the chair just named; he read his paper on the passivity of iron before the Natural History Society of Basle in 1835; he discovered ozone in 1839 and worked at it until 1860; and his discoveries of guncotton and of collodion were made between 1846 and 1853.

The long studied and puzzling problems connected with ozone and "antozone," that occupied so much of his life are here set forth with a minuteness not elsewhere found; the claims of others to the discovery of guncotton are dwelt upon fully, and it is significant to read that Schönbein reaped about $20,000 from his discovery, while Alfred Nobel gained no less than $10,000,000.

Schönbein enjoyed the friendship of nearly all his contemporaries in the physical sciences; his correspondence with Faraday forms a volume edited by Kahlbaum and Darbishire and published at London in 1899.

The volumes under review form so important a contribution to the history of chemistry that no library can well afford to be without them. H. CARRINGTON BOLTON.

THE ELEMENTARY PRINCIPLES OF CHEMISTRY. By A. V. E. YOUNG. 12 mo. xiv + 252 pp. New York: D. Appleton & Co. 1901. Price, $1.20.

The author of this book desires "that the first notion of a topic should come to the student through his own observation" and provides, with this end in view, a relatively large amount of laboratory work, more of which is quantitative in character than is usual in elementary courses.

In a pamphlet entitled "Suggestions to Teachers," which accompanys the book, Professor Young points out the advantages of the plan which, he advocates, indicates the amount of time required—eight hours per week for thirty-five weeks,—and gives helpful advice to teachers. The greater part of the time is, evidently, to be devoted to the laboratory work.

The introductory chapters discuss matter, energy, chemical and physical properties, the fundamental laws of chemical action, equivalent and combining weights and methods for obtaining

them, equations, the relation between the volume, pressure, and temperature of gases, etc. Then follows a chapter on the atomic and other theories, the distinction between the theories and the facts, which they are intended to explain being clearly shown. The author has been very successful in presenting, with a limited use of theoretical considerations, the prevailing views of chemists.

The remaining two-thirds of the book give a clear, and sufficiently full description of twenty-five elements, and some of their compounds, the order of treatment being that of their increasing combining weights. The writer believes that this part of the subject would have been of more value, if enough elements had been described to show more clearly the relation of elements belonging to the same groups.

Part second, which may also be obtained separately, contains directions for work in the laboratory. Illustrations of twelve distinguished chemists and physicists are an attractive feature of the book.

L. B. HALL.

BOOKS RECEIVED.

The Elementary Principles of Chemistry. By A. V. E. Young. New York : D. Appleton & Co. 1901. xiv + 106 pp. Price, $1.20.

Suggestions to Teachers ; designed to accompany "The Elementary Principles of Chemistry." By A. V. E. Young. New York : D. Appleton & Co. 1901. 48 pp.

Pure Air, Ozone and Water. A practical treatise of their utilization and value in oil, grease, soap, paint, glue, and other industries. By W. B. Cowell. London : Scott, Greenwood & Co.; New York : D. Van Nostrand Co. 1900. 85 pp. Price, $2.00.

The Testing and Valuation of Raw Materials used in Paint and Colour Manufacture. By M. W. Jones, F.C.S. London : Scott, Greenwood & Co.; New York : D. Van Nostrand Co. 1900. 88 pp. Price, $2.00.

The Manufacture of Lake Pigments from Artificial Colours. By Francis H. Jennison. London : Scott, Greenwood & Co.; New York : D. Van Nostrand Co. 1900. 136 pp. Price, $3.00.

Iron Corrosion. Anti-fouling and Anti-corrosive Paints. By Louis Edgar Andés. Translated from the German by Charles Salter. London : Scott, Greenwood & Co.; New York : D. Van Nostrand Co. 1900. viii + 275 pp. Price, $4.00.

Glue and Glue Testing. By Samuel Rideal. D.Sc.Lond. London : Scott, Greenwood & Co.; New York : D. Van Nostrand Co. 1900. viii + 144 pp. Price, $4.00.

(1) An Apparatus for the Determination of the Melting-Point of Fats.

By Frank T. Shutt and H. W. Charlton. Canadian Experiments with Nitragin for Promoting the Growth of Legumes. By Frank I. Shutt and A. T. Charron. From the *Transactions of the Royal Society of Canada*. Second Series. 1900–1901. Vol. VI, Section III.

Report of the Connecticut Agricultural Experiment Station for the Year ending October 31, 1900. Part III. Peach Foliage and Fungicides — Literature of Plant Diseases — Fertilizers for Forcing — House Crops — Chestnut Grafting — Insect Notes — Tobacco Experiments — Protection of Shade Trees — Cattle Foods. New Haven, Conn. 169 pp. 16 plates.

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On the Mode of Occurrence of Ruby in North Carolina. By J. W. Judd and W. E. Hidden, with crystallographic notes by J. H. Pratt. From the *American Journal of Science*, Vol. VIII. 13 pp.

Talc and Pyrophyllite Deposits in North Carolina. By Joseph Hyde Pratt. North Carolina Geological Survey. Economic Papers, No. 3. 29 pp.

The Farmer's Vegetable Garden.—Bulletin No. 61. 16 pp. The Market Classes of Horses.—Bulletin No. 62. 12 pp. Seed Corn and Some Standard Varieties for Illinois.—Bulletin No. 63. 28 pp. Treatment of Oats for Smut.—Bulletin No. 64. 16 pp. Construction and Care of Earth Roads.—Bulletin No. 65. 21 pp. University of Illinois Agricultural Experiment Station, Urbana, Ill.

Select Methods in Food Analysis. By Henry Leffmann, A.M., M.D., and William Beam, A.M., M.D. Philadelphia : P. Blakiston's Son & Co. 1901. 383 pp. Price, $2.50.

Orchard Experiments. Bulletin No. 73. Hatch Experiment Station of the Massachusetts Agricultural College, Amherst, Mass. March, 1901. 15 pp.

Eggs and Their Uses as Food. By C. F. Langworthy, Ph.D. Farmers' Bulletin No. 128. U. S. Department of Agriculture, Washington, D. C. 1901. 32 pp.

Summer Forage Crops. Bulletin No. 72. Hatch Experiment Station of the Massachusetts Agricultural College, Amherst, Mass. March, 1901. 16 pp.

Fertilizers—Truck Shipments—Sweet Potatoes. Vol. 22, No. 4. The Bulletin of the North Carolina State Board of Agriculture, Raleigh, N. C. April, 1901. 36 pp.

Thirteenth Annual Report of the Hatch Experiment Station of the Massachusetts Agricultural College. January, 1901. Public Document No. 33. 132 pp.

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Atoms and Energies. By D. A. Murray. New York: A. S. Barnes & Company. 1901. 202 pp. Price, $1.25.

A Mica-Andesite of West Sugarloaf Mountain, Boulder County, Colorado. Some Relations of Tetrahedral Combinations to Crystalline Form. By John Charles Blake. *Proceedings of the Colorado Scientific Society*, Vol. 7. pp. 13–36. Denver, Colo.

The Chemistry of the Jaborandi Alkaloids. By H. A. D. Jowett. The Pharmacology of the Jaborandi Alkaloids. By C. R. Marshall. Remarks on Extractum Jaborandi Liquidum. By H. A. D. Jowett and C. R. Marshall. Reprinted from the *British Medical Journal*, Oct. 13, 1900. 13 pp.

A New Admixture of Commercial Strophanthus Seed. By Pierre Élie Félix. Perrédès. 12 pp. Researches on Morphine, Part II. By S. B. Schryrer and Frederic H. Lees. 18 pp. The Constitution of Pilocarpine, Part II. By H. A. D. Jowett. 23 pp. From the Wellcome Chemical Research Laboratories, Frederick B. Power, Director, 6 King St., Snow Hill, London, E. C.

Induction Coils. How to Make, Use, and Repair Them. By H. S. Norrie (Norman H. Schneider). Second edition, revised and much enlarged. New York: Spon & Chamberlain. 1901. xi + 269 pp. Price, $1.00.

American Handy-Book of the Brewing, Malting, and Auxiliary Trades. Copiously illustrated. By Robert Wahl and Max Henius. Chicago: Wahl & Henius, 294 S. Water St. xv + 1266 pp. Price, $10.00.

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An Introduction to the Study of Chemistry. By Ira Remsen. Sixth Edition, revised and enlarged. New York: Henry Holt and Company. 1901. xxii + 460 pp. Price, $1.12.

Chemical Lecture Experiments. By Francis Gano Benedict, Ph.D. New York: The Macmillan Co. 1901. xiii + 436 pp. Price, $2.00.

Lectures on the History of the Development of Chemistry Since the Time of Lavoisier. By Dr. A. Ladenburg. Translated from the Second German Edition of Leonard Dobbin, Ph.D., with additions and corrections by the author. Edinburgh: Published by The Alembic Club. Edinburgh Agent: William F. Clay, 18 Teviot Place; London Agents: Simpkin, Marshall, Hamilton, Kent & Co., Ltd. 1900. xvi + 373 pp.

A Short Manual of Inorganic Chemistry. By A. Dupré, Ph.D., and H. Wilson Hake, Ph.D. Third edition, thoroughly revised and partly rewritten, with special reference to the periodic law. London: Charles Griffin & Co., Limited; Philadelphia: J. B. Lippincott Company. 1901. xv + 391 pp. Price, $3.00.